REPORT 1186

FORMATION AND COMBUSTION OF SMOKE IN LAMINAR FLAMES [1]

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SUMMARY

The nature and formation of smoke and its combustion were investigated. Smoke, which consists of tiny mesomorphous crystals tightly packed into popcorn-ball-like particles that agglomerate to give filaments, was found to contain about 5 percent of the hydrogen originally present in the fuel.

Factors affecting smoke formation were studied in both diffusion flames and premixed Bunsen flames. The rates at which hydrocarbon types could be burned without smoking decreased in the approximate order: n-paraffins>isoparaffins>cycloparaffins $\gtrsim$ olefins > cycloolefins $\geq$ diolefins $\sim$ alkynes > n-alkylbenzenes. It is suggested that smoking tendency increases with increasing stability of the carbon skeleton of the molecule, as determined by relative bond strengths. Smoking tendencies within the n-paraffin series increased with molecular weight, presumably because of changes in diffusion rates. Increasing the laminar air flow around a flame decreased its smoking tendency, but eventually a limiting smoke-free fuel rate was found for diffusion flames and a limiting primary fuel-air ratio was found for Bunsen flames. Moreover, the smoking-point fuel-air ratio of a premixed flame deprived of secondary air was only half that of a similar flame burning in "still" air. Oxygen-enrichment of the surrounding air, or substitution of argon for nitrogen in this "air," decreased smoking tendency for fuels of moderate smoking tendency. For some fuels of greater smoking tendency, however, moderate oxygen-enrichment or argon substitution (both of which increase flame temperature) increased smoking tendency. Increasing the fuel rate to a Bunsen flame decreased the smoking-point fuel-air ratio, while preheating the fuel or fuel-air mixture had no effect. For diffusion flames, smoking tendency was linearly related to reciprocal pressure for the range ½ to 20 atmospheres, but for premixed flames pressure is reported to have no effect; these facts again suggest the importance of diffusion rates.

A critical survey of the literature pertaining to the mechanism of smoke formation was made. A probable mechanism appears to consist of initial dehydrogenation steps, followed by decomposition to acetylene and hydrocarbon fragments, which then undergo simultaneous polymerization and dehydrogenation to form smoke.

Considerable quantities of finely divided smoke could be burned in the outer reaction zone or hot-gas mantle of a flame; however, if the smoke reached this outer mantle at such a great rate that it was clumping into soot particles, such particles were only partially consumed before passing out of the flame. The smoke-burning ability of a flame was apparently related to the oxygen available through direct supply or diffusion processes.

INTRODUCTION

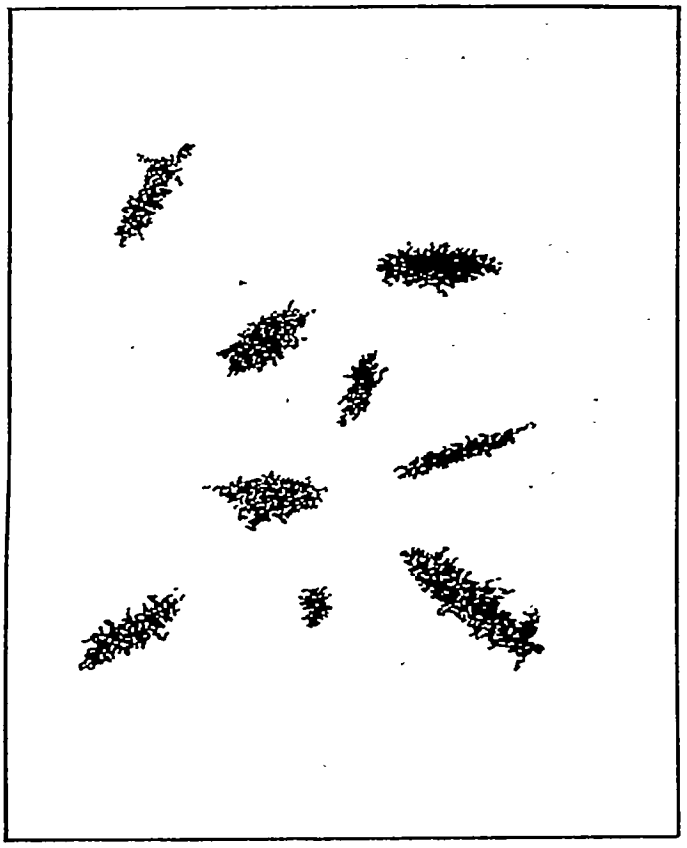
One troublesome problem in turbojet combustion-chamber operation has been the formation of smoke and other residues. While such products do not affect combustion efficiency appreciably, they do produce undesirable side effects such as badly smoking engines, fouled fuel nozzles, and blocked air ports. Full-scale tests on combustion chambers have shown that several variables affect smoke formation. It increases with combustion-chamber pressure or fuel temperature, but decreases as the air temperature is raised or as more air is forced into the primary burning zone. Smoking tendency in combustors is strongly influenced by fuel composition and volatility and by fuel-air ratio.

The physical and chemical processes involved in the mixing and combustion of fuel in a combustion chamber are complex. The turbojet combustor operates fuel-lean over-all, at equivalence ratios of the order of 0.1 to 0.3. However, since fuel is introduced locally while air is introduced throughout the combustion chamber, rich zones exist within the chamber. Flame types may vary from lean premixed Bunsen flames to pure diffusion flames in which fuel vapor and air interdiffuse and burn at a common interface. Because of the complex nature of the processes that occur in combustion chambers, no single set of bench-scale experiments answers questions that arise.

This report contains information on several related projects, which, considered together, give a coherent picture of the general principles of smoke formation and combustion in flames of various types. Smoking tendency is presented for gaseous diffusion flames, wick lamps, and premixed Bunsen flames for the following variables:

(1) Fuel type (38 pure hydrocarbons)
(2) External air-flow rate
(3) Oxygen-enrichment of external air ($O_2/(O_2+N_2)=0.21$ to 0.45)
(4) Substitution of argon for nitrogen in external oxidant ($O_2/(O_2+A)=0.21$ to 0.45)
(5) Fuel temperature (room temp. to 190° C) or primary mixture temperature (room temp. to 500° C)
(6) Pressure (½ to 20 atm)

[1] Supersedes NACA RM's E51E15, "Combustion of Smoke in Diffusion and Bunsen Flames," by Thomas P. Clark, 1951; E52G24, "Influence of External Variables on Smoking of Benzene Flames," by Thomas P. Clark, 1952; E52I22, "Variations in Smoking Tendency Among Low Molecular Weight Hydrocarbons," by Rose L. Schalla and Glen E. McDonald, 1952; E52I26, "Examination of Smoke and Carbon from Turbojet-Engine Combustors," by Thomas P. Clark, 1952; E53E05, "Effect of Pressure on the Smoking Tendency of Diffusion Flames," by Rose L. Schalla and Glen E. McDonald, 1953; E53J12, "Effect of Diffusion Processes and Temperature on Smoking Tendencies of Laminar Diffusion Flames," by Rose L. Schalla, 1953; and E54E03, "Effect of High Pressure on Smoking Tendency of Diffusion Flames," by Glen E. McDonald and Rose L. Schalla, 1954.



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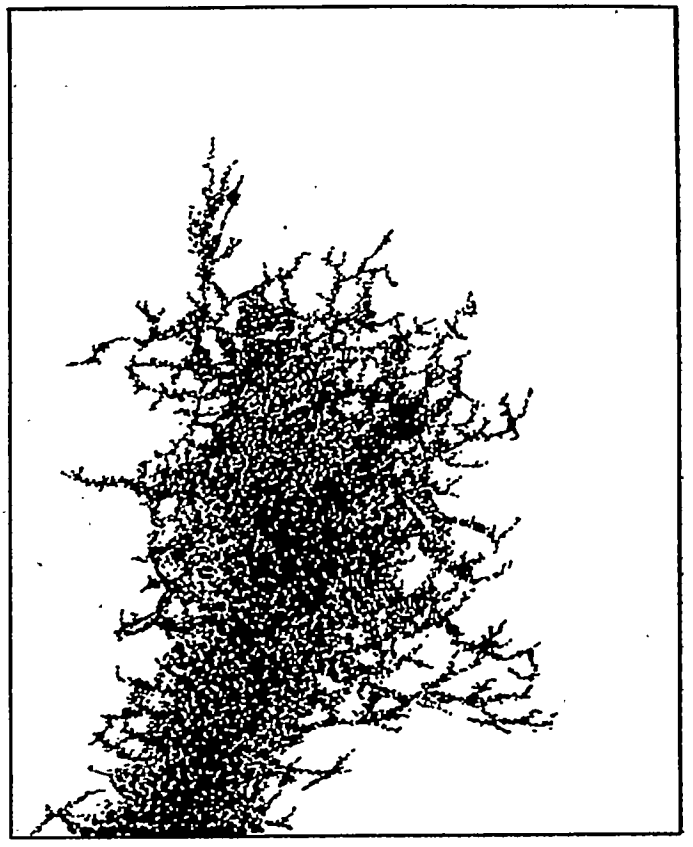

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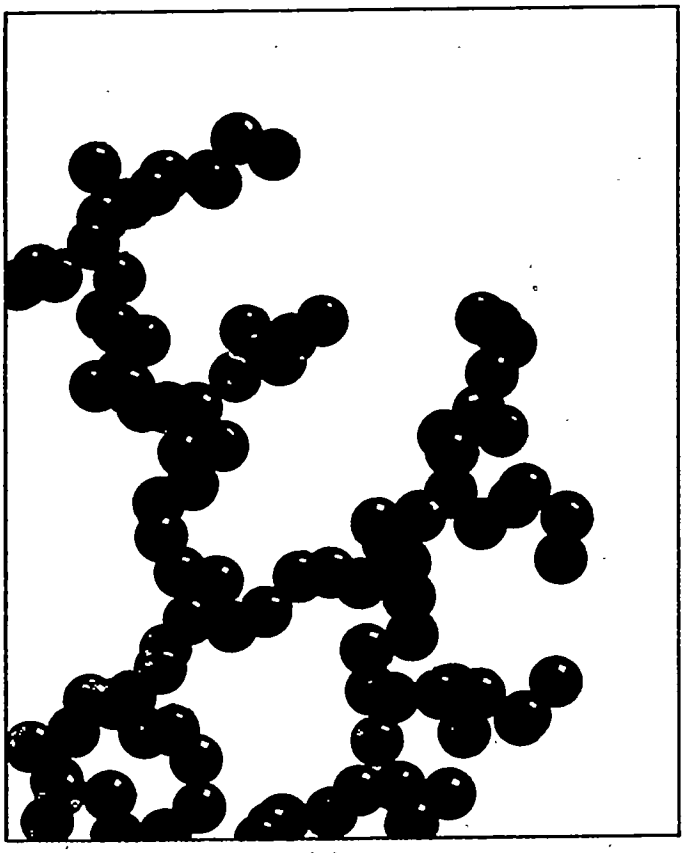

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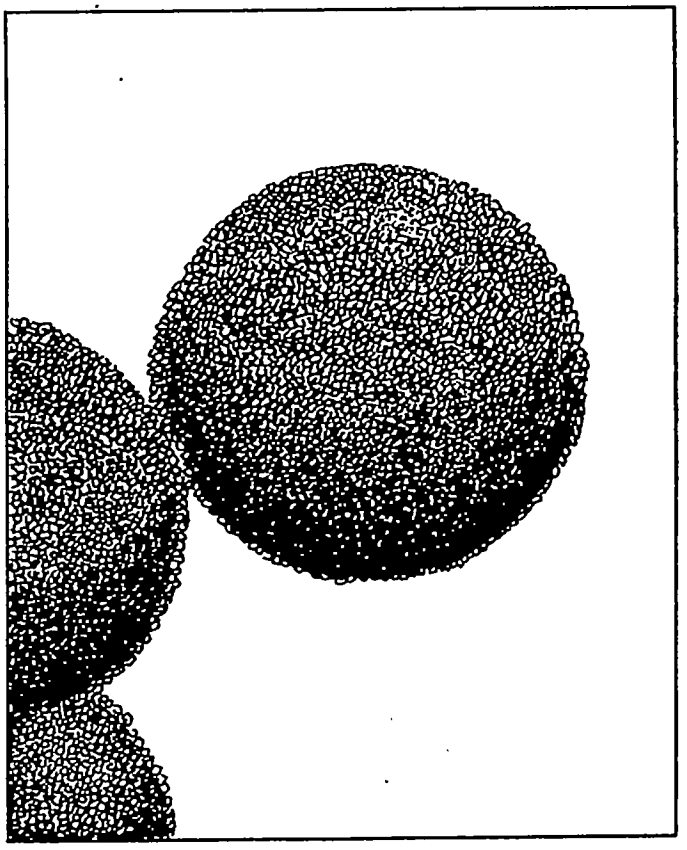


(d)

(a) Particles of soot. X100.
(b) Edge of soot particle. X1000.
(c) Edge of soot particle showing chain-like structure of carbon particles. X100,000.
(d) Nature of packed crystallite structure making up carbon particle. X1,000,000.

FIGURE 1.—Diagrammatic sketches of appearance of carbon black and soot at various magnifications.

Several correlations of some of these parameters with smoking tendency and a possible mechanism of smoke are considered. Studies were also made of the smoke-burning properties of the primary and secondary reaction zones of ethylene-air flames over a range of fuel-air ratios. Smoke was burned both as homogeneous fuel-air-smoke mixtures and as heterogeneous filaments of concentrated smoke.

PHYSICAL AND CHEMICAL NATURE OF SMOKE

Luminous hydrocarbon flames, as distinct from so-called nonluminous ones, emit a yellow radiation that has a blackbody energy-wavelength distribution characteristic of radiating solids. The only possible solid products from hydrocarbon combustion are either carbon or materials containing very high percentages of carbon. That such materials can be obtained from luminous flames is confirmed by the deposits formed on a cold probe passed through such a flame. Under some conditions the solids are released from luminous flames as smoke.

The smoke from a burning hydrocarbon appears normally as a dark gray streak or cloud. When a portion of this smoke is allowed to impinge on a microscope slide, it deposits as a structureless film of carbon black. If the flame smokes heavily and the smoke-air mixture is swirled and mixed before collection, the smoke tends to coagulate into small particles of soot. At a magnification of 100, these particles are seen to have a flocculent, lace-like structure (fig. 1 (a)); at 1000 magnification, the lace-like structure seems to be made of tiny particles (fig. 1 (b)). Examination of the edge of such a soot particle in an electron microscope at 100,000 magnification reveals that it is made up of strings and clusters of roughly spherical particles of a nearly uniform size (fig. 1 (c)). The diameters of these spherical particles may vary from 0.01 to 1.0 micron. The particles may cling together by means of electrostatic attraction or may actually be attached to each other by means of necks (ref. 1).

X-ray diffraction studies of hydrocarbon smokes and amorphous carbon blacks (refs. 2 and 3) reveal that the spherical particles observed in the electron microscope are made up of agglomerates of tiny mesomorphous crystals. These crystals, or crystallites, have major edge dimensions of approximately 20 angstroms. The crystallites are packed together in a random fashion, much like a popcorn-ball structure, to form the spherical particle (fig. 1 (d)). A typical analysis shows 92.6 percent carbon and 0.8 percent hydrogen; the remainder is believed to be oxygen. This hydrogen content is only about 5 percent of that in the hydrocarbon. The spherical particles, therefore, consist almost completely of carbon and are the intermediate structural units of soots, smokes, and carbon blacks. These small spherical particles will be called carbon particles.

The atomic structure of the crystallites making up the carbon particles has been determined from an analysis of X-ray diffraction patterns (refs. 2 to 4). The crystallite consists of several layers of carbon atoms lying in distorted hexagonal crystal lattices. The distortion of the crystal lattice is attributed to the presence of the residual hydrogen mentioned previously (see ref. 4). The layers of carbon atoms are parallel to each other and spaced in a fashion characteristic of graphite. However, the planes are not oriented parallel to each other along the other two axes as is the case for graphite. A graphite crystallite might be compared to a deck of playing cards oriented as they are when stored in a box. A smoke crystallite might be compared to the same deck of cards put on a spindle, with the edges of the cards turned at random angles to each other.

Electron micrographs of smoke of a turbojet fuel obtained from a wick lamp and from the exhaust of a turbojet engine are shown in figures 2 (a) and (b), respectively. These smokes are similar, except that the smoke that passed through the combustion chamber (fig. 2 (b)) is partially burned and reduced in size.

Carbon deposits on the interior surfaces of combustion chambers differ from diffusion-flame smokes. Figure 2 (c) shows a portion of a soot-like carbon deposit found near the fuel nozzle, and 2 (d) shows the edges of two flakes of vitreous coke deposit found on the combustor liner where unvaporized fuel impinged. (The diffuse material between the flakes is a scattering of out-of-focus smoke particles.) As can be seen in these figures, the soft carbon has some of the chain-like character of smoke, whereas the hard deposit appears to be amorphous. The hydrogen-carbon ratios are indicated in the figure legend.

FACTORS AFFECTING SMOKE FORMATION

FUEL TYPE

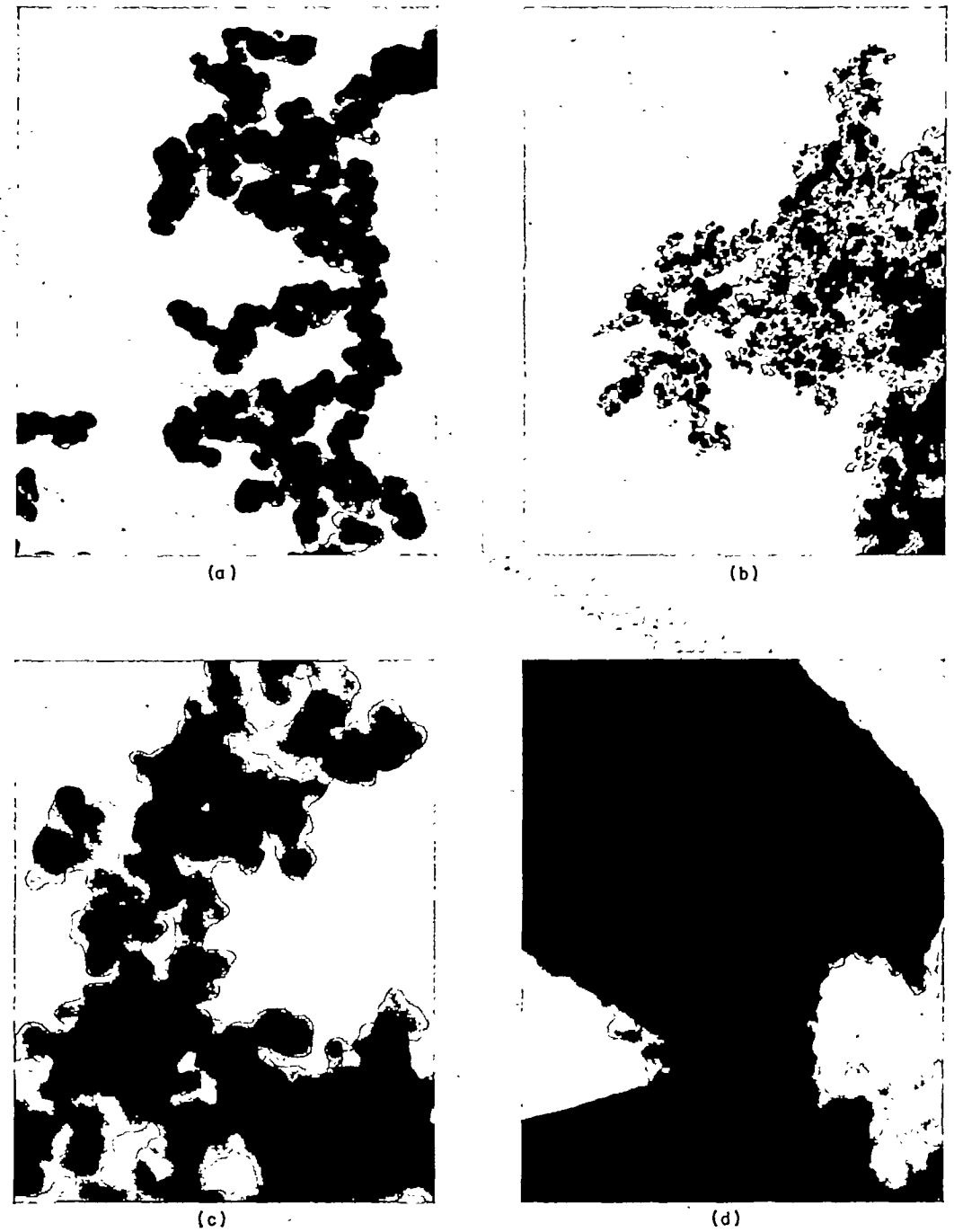
Diffusion flames.—A systematic survey of the smoking tendency of various hydrocarbon fuel types was conducted at a pressure of 1 atmosphere and at room temperature. Altogether 38 pure hydrocarbons were burned in still air as diffusion flames from simple burners such as those in figure 3. The apparatus shown in figure 3 (a) was used for gaseous fuels and that in 3 (b) for liquid fuels. Liquid fuels could be vaporized and burned in the gas phase as shown in figure 3 (c). A visual observation was used to detect the first smoke issuing from the flame. The rate in grams per second at which a hydrocarbon could be burned smoke-free was used as the criterion of its smoking tendency.

In figure 4 the smoke-free burning rates are plotted against the number of carbon atoms in the molecule for various hydrocarbon classes. The following is approximately the decreasing order of smoke-free fuel rate (increasing order of smoking tendency): *n*-paraffins $>$ isoparaffins $>$ cycloparaffins $\gtrsim$ olefins $>$ cycloolefins $\geq$ diolefins $\sim$ alkynes $>$ *n*-alkylbenzenes. The following individual variations are of particular interest:

(1) For *n*-paraffins the smoke-free fuel rate decreases smoothly with increasing molecular weight.

(2) The 1-olefin curve passes through a minimum in the vicinity of propene and 1-butene.

(3) Cyclopropane $\leq$ propene.



(a) Wick-lamp smoke of jet-engine fuel. H/C, 0.008.
(b) Smoke collected from exhaust of combustor. H/C, 0.008.
(c) Edge of flake of soft carbon from dome of combustor. H/C, 0.025.
(d) Flakes of pulverized hard carbon from liner of combustor. H/C, 0.018.

FIGURE 2.—Electron micrographs of various carbon structures associated with smoke and carbon in jet-engine combustors. X50,000.

If the reciprocal of the equivalent gaseous fuel flow in milliliters per second is plotted against the number of carbon atoms in a molecule, straight lines result for the various homologous series (fig. 5). (Note, however, that two lines are obtained for olefins, one for the lower and the other for higher molecular weights.) Extrapolation of these lines might be used to estimate smoking tendencies of higher molecular weight hydrocarbons in the absence of experimental data.

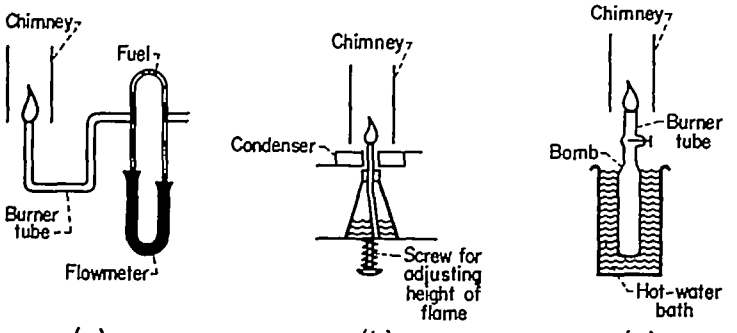
Several methods of predicting or explaining the variation in smoking tendency among different fuel types have been proposed. The following equation, based on the oxygen requirements of diffusion flames, was developed by Minchin (ref. 5) to predict the maximum smoke-free flame height h (the constants apply only for his apparatus):

$$h=\frac{(x+3)^2}{36.1\,xy+54.9-26.25x^2}$$

where

x moles of combustion products (CO_2+H_2O) per mole of fuel
y moles of oxygen needed to burn one mole of fuel

This equation correctly predicts qualitative trends for hydrocarbons within a class, but it does not predict the differences that are observed among isomers.



(a) Gases. (b) Liquids. (c) Liquids.

FIGURE 3.—Diagram of apparatus.

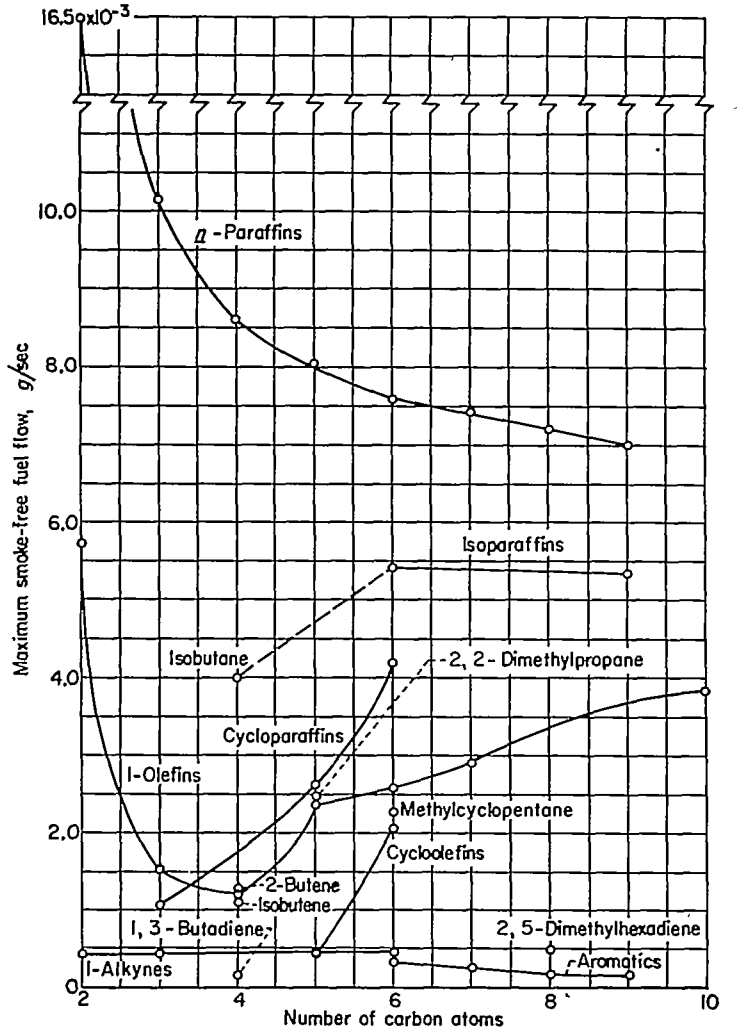


FIGURE 4.—Variation of maximum smoke-free fuel flow with number of carbon atoms.

The relation between the tendency to smoke and the carbon-hydrogen ratio of the compound is discussed in reference 6, which indicates that, in general, compounds of higher carbon-hydrogen ratio show a higher smoking tendency. This concept has been used to predict qualitative trends in combustor coke deposition (ref. 7). Like Minchin's equation, however, it does not explain the differences among isomers. Consequently, reference 6 attributes the difference among isomers to the fact that a more compact molecule has a higher smoking tendency (e. g., isobutane > *n*-butane).

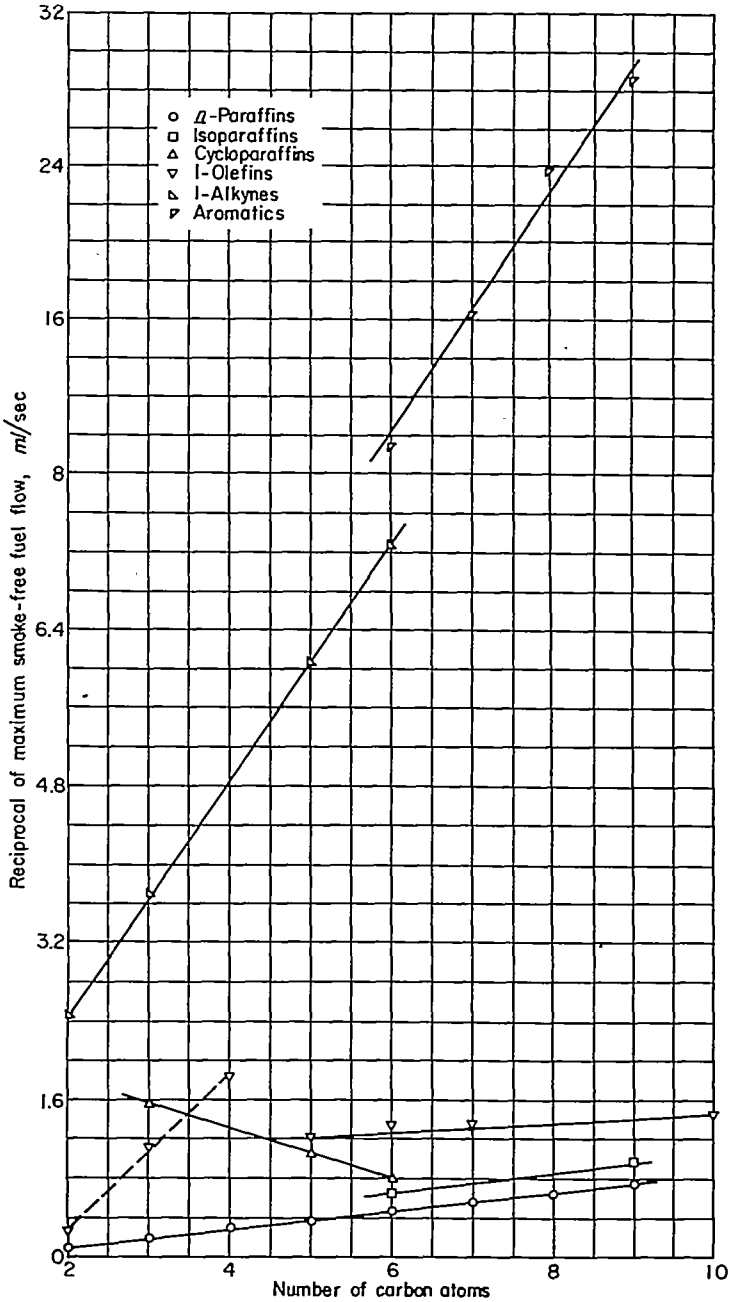
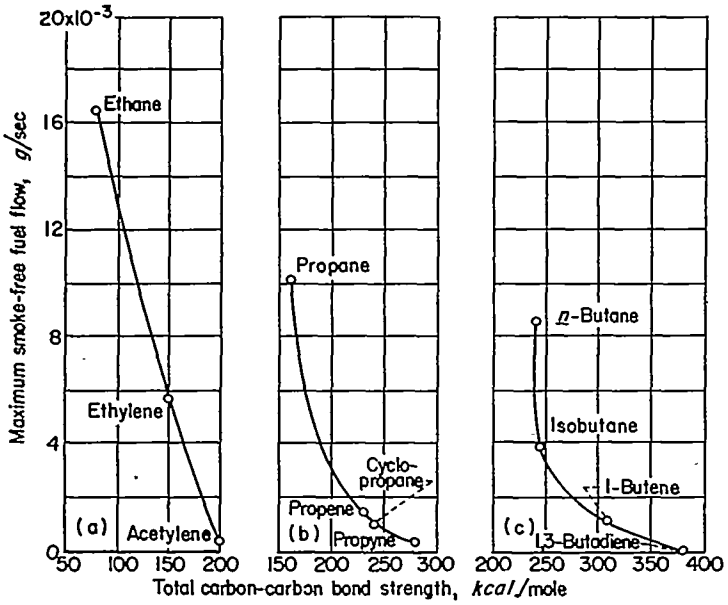


FIGURE 5.—Variation of reciprocal of maximum smoke-free fuel flow with number of carbon atoms.

Attempts were made in this investigation to correlate smoking tendencies with other properties of fuels, such as diffusion coefficients, boiling point, density, rate of pyrolysis, and rate of polymerization. Changes in diffusion coefficient satisfactorily explain the differences in smoking tendency in the same homologous series of compounds (e. g., *n*-paraffins); but the variations in smoke formation among the homologous series, among structural isomers, and within the olefin series are not satisfactorily correlated with changes in either diffusion coefficient or any other of the previously mentioned parameters.

It has been proposed (as will be discussed later) that hydrogen is stripped from the carbon skeleton during combustion under smoking conditions. The stabilities of the carbon chain or skeleton may therefore be important in considering relative smoking tendencies. This proposal is admittedly

speculative, but it seems more consistent than the other types of correlation. Figure 6 shows that, among compounds of the same number of carbon atoms, the smoke-free fuel rate decreases with unsaturation: ethane > ethylene > acetylene. The change in structure from single- to double- to triple-bonded carbon atoms in these compounds is accompanied by an increase in carbon-carbon bond strengths from approximately 80 to 150 to 200 kilocalories per mole, respectively (ref. 8). The variation in bond strengths among the isomeric paraffins is less definite, but isoparaffins may possess about 5 kilocalories per mole more total carbon-carbon bond strength than *n*-paraffins (ref. 9). Data on heats of formation also indicate that isoparaffins are more stable than the *n*-paraffins (ref. 10). Stability increases with increased branching.



(a) Compounds of two carbon atoms. (b) Compounds of three carbon atoms. (c) Compounds of four carbon atoms.

FIGURE 6.—Variation of maximum smoke-free fuel flow with carbon-carbon bond strength.

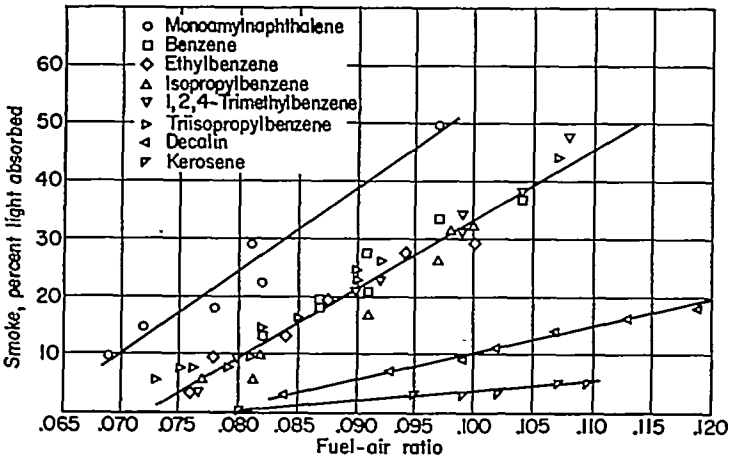
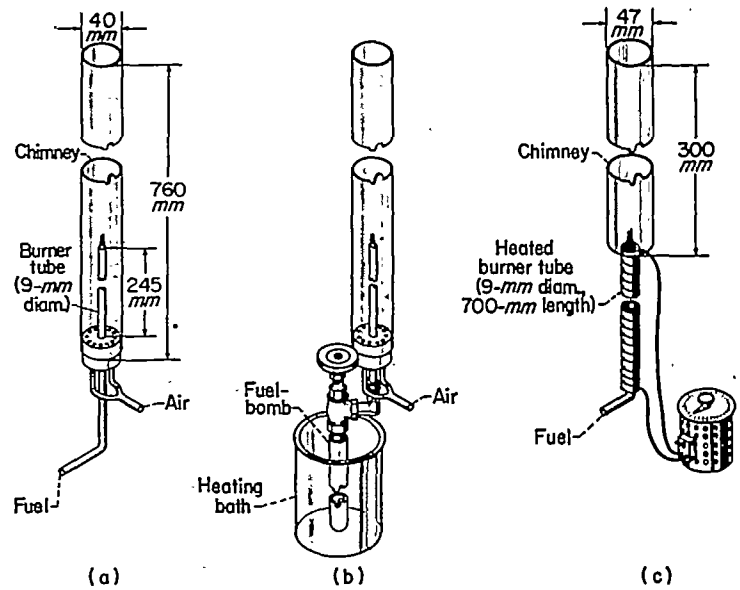


FIGURE 7.—Variation of smoke with fuel-air ratio for several fuels burning as Bunsen flames. Air flow, 4.1 liters per minute. (Data from ref. 13.)

A comparison of carbon-chain stabilities was not made among homologous compounds of different numbers of carbon atoms. Such a comparison is meaningless, since any variation in ease of breaking the carbon-carbon bonds is overshadowed by the additional increase in the amount of carbon existing in the compound. In the paraffin series, for example, the carbon-carbon bonds in *n*-octane may be weaker than those in ethane (ref. 8), but there would be four times as many carbon atoms present in *n*-octane. Estimation of the carbon-carbon bond energy per bond did show qualitative correlation with smoking tendency.

Undoubtedly, other factors adding to the stability of the carbon chain or skeleton must be taken into consideration. One of those factors is hyperconjugation. Wheland (ref. 11) reports that such compounds as propene and butene are stabilized as a result of hyperconjugation, and that hyperconjugation in propene produces a resonance energy of about the same order of magnitude as does the conjugation between two double bonds, as in butadiene. It is possible that the apparent minimum in the olefin curve around propene and butene (fig. 4) results from the increased stability of these two compounds. The effect is probably carried over to a lesser extent in some of the olefins of higher molecular weight.

Some additional explanation is also necessary to account for the trends of the cycloparaffins. Ring stability increases from cyclopropane to cyclopentane, and yet the rate of fuel burned smoke-free also increases. The low rate for cyclopropane may be explained on the basis that cyclopropane readily isomerizes to propene (ref. 12) at temperatures encountered when entering the flame. Consequently, the fuel-flow rate of cyclopropane should be close to that of propene. This agreement is shown experimentally in figure 4.



(a) Burner tube. (b) Apparatus modified for vaporized liquid fuels. (c) Apparatus modified for preheating fuels.

FIGURE 8.—Diagram of apparatus.

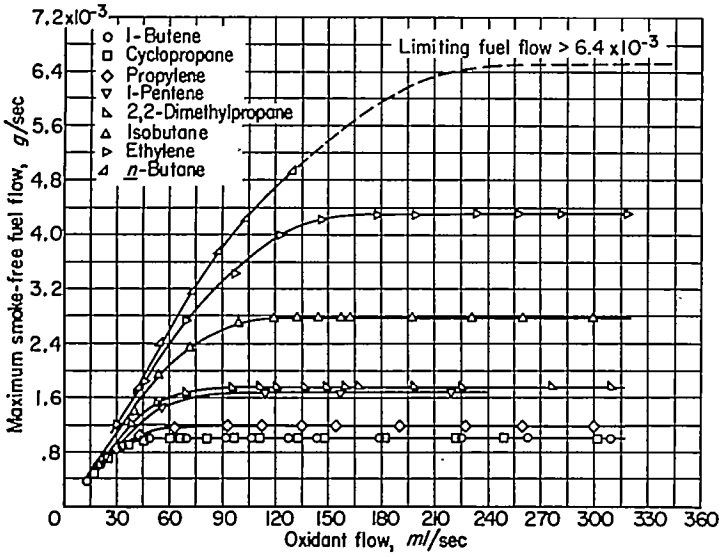


FIGURE 9.—Variation of smoke-free fuel flow with air flow past flame.

If it is permissible to conclude from the preceding discussion that increases in the stability of the molecule accompany increases in smoking tendencies, a possible step in the mechanism for the formation of smoke may be deduced. The carbon-hydrogen bond strength is approximately 100 kilocalories per mole (ref. 11), as compared with the carbon-carbon bond strengths of 80, 150, and 200 kilocalories for single, double, and triple bonds, respectively. Thus, in the saturated compounds the carbon-carbon bonds may be broken more readily than the carbon-hydrogen bonds, but in unsaturated compounds the reverse is true. A dehydrogenation process may, therefore, be favored as the stability of the carbon skeleton increases. Removal of the hydrogen atoms by thermal and oxidative processes probably leaves behind partially dehydrogenated skeletons of carbon atoms that might polymerize to form smoke.

Premixed flames.—Variations in smoke formation of various hydrocarbons have been measured in Bunsen flames by Ebersole and Barnett (ref. 13). A light beam was passed through the chimney in which the smoke was issuing from the flame, and a photoelectric cell was used to determine the amount of light absorbed as a measure of the smoke formation. The air flow being premixed with the fuel was held constant at 4.1 ± 0.1 liters per minute, and the fuel flow increased to give the fuel-air ratios indicated in figure 7. Paraffins, cycloparaffins, and olefins could not be made to smoke under the conditions of this experiment. Consequently, these fuels would appear to be less smoky than the aromatics and other fuels shown in figure 7, where the percentage of light absorbed is plotted against fuel-air ratio. The aromatics all show higher smoking tendencies than decalin (a bicycloparaffin) and kerosene (a petroleum cut predominantly paraffinic). To this extent the results are similar to those described previously for diffusion flames.

OXYGEN SUPPLY

Diffusion flames.—External air-flow rate: The effects of external air-flow rate on maximum smoke-free fuel rate for eight pure hydrocarbons were investigated in the apparatus shown in figure 8. A burner tube 9 millimeters in diameter was enclosed by a pyrex tube 40 millimeters in diameter and

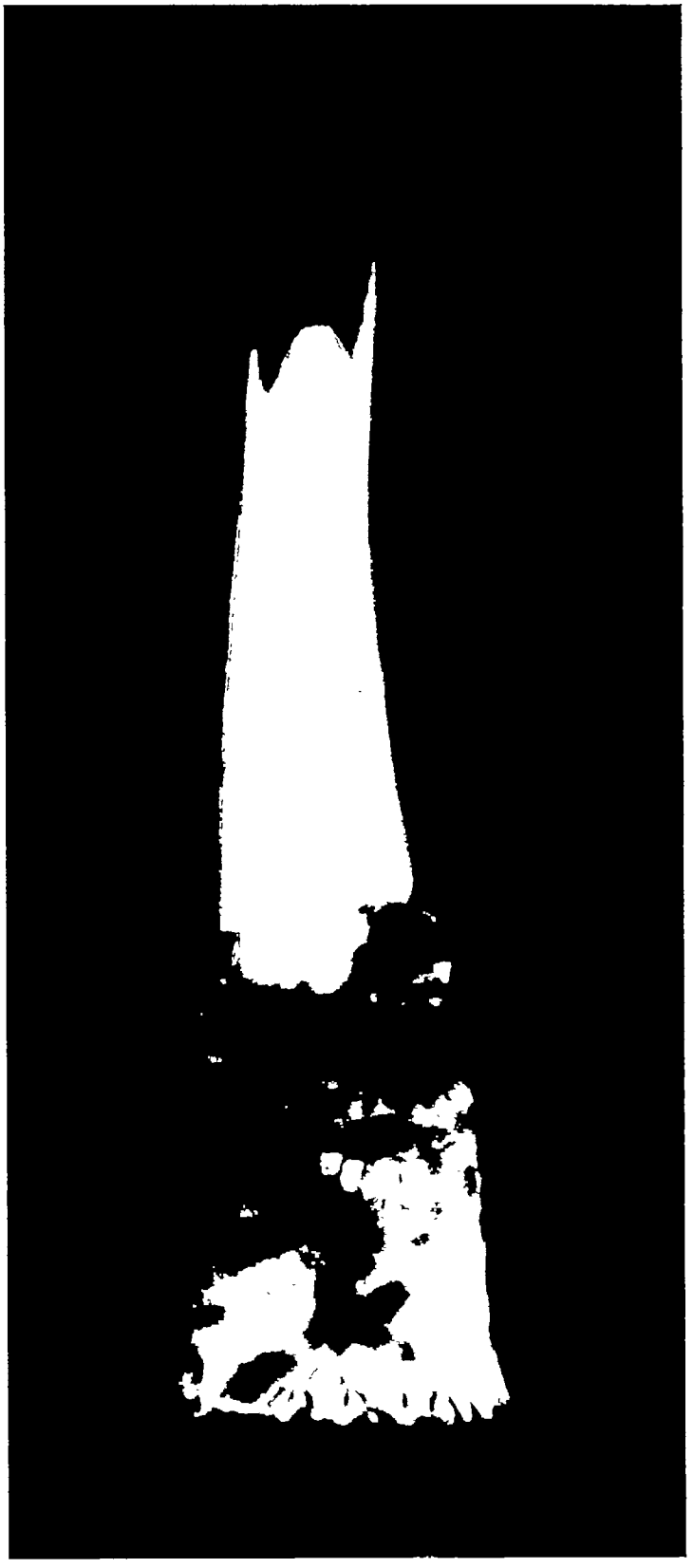


FIGURE 10.—Propene diffusion flame burning in 50 percent oxygen, showing formation of solid carbon at base of flame.

760 millimeters high. All the air supplied to the flame was admitted through holes in a cylindrical chamber sealed into the base of the pyrex tube. Both the fuel and air were metered before entering the tubes. For 1-pentene, a heated bomb (fig. 8 (b)) was used to vaporize the fuel; the fuel-flow rate was determined by weight loss.

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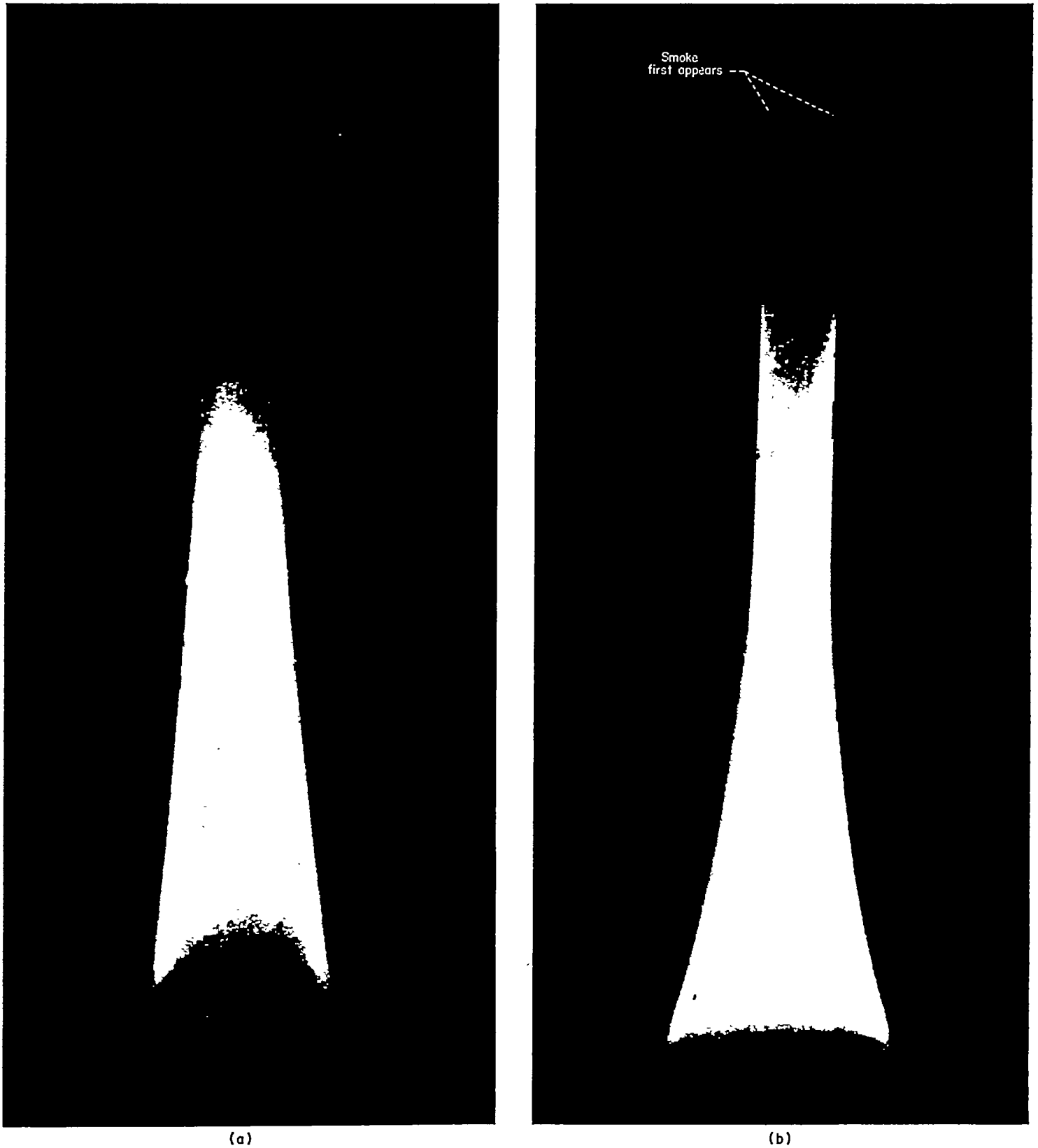
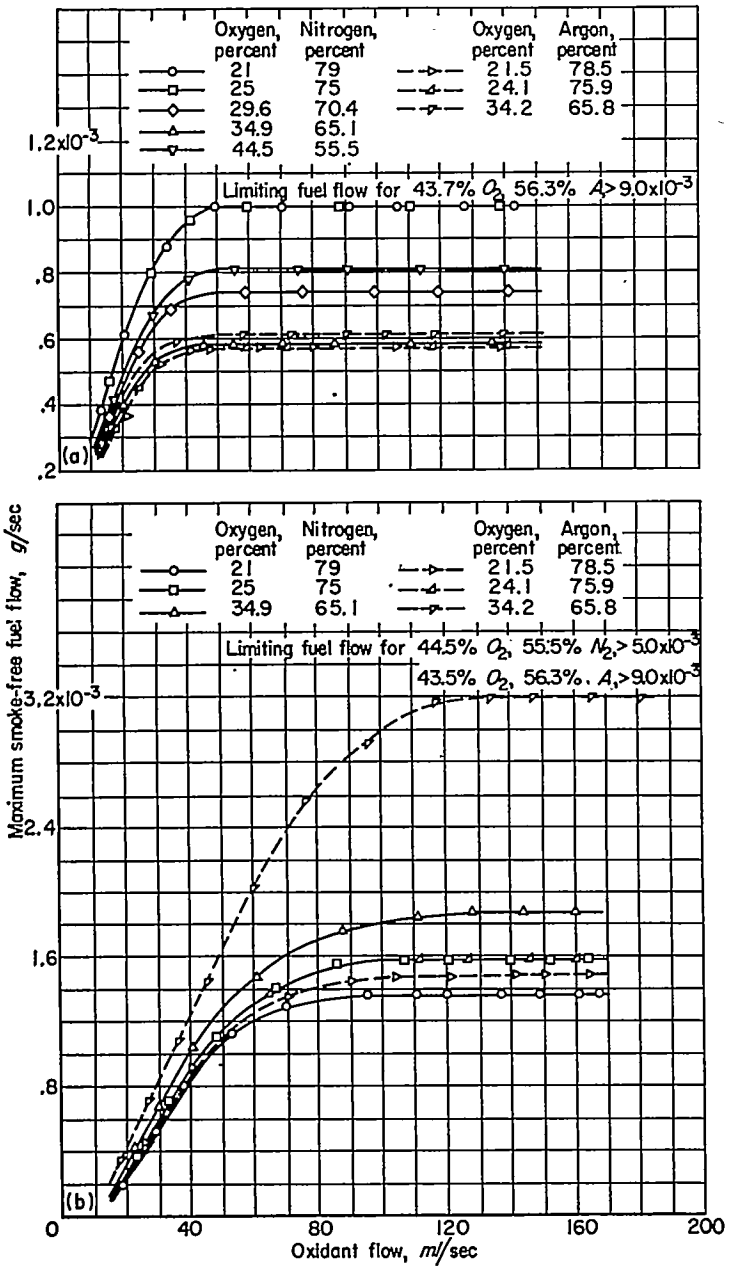


(a) In air.

(b) In 35 percent oxygen, 65 percent nitrogen.

FIGURE 11.—Diffusion flames.



(a) 1-Butene.

(b) 2,2-Dimethylpropane.

FIGURE 12.—Variation of maximum smoke-free fuel flow with oxygen-enriched mixtures.

Figure 9 shows that, as the air flow past the flame is increased, the smoke-free fuel flow at first increases proportionally; however, a limiting fuel flow is shortly reached, and additional increases in the air flow do not permit further increase in the fuel flow for smoke-free burning. The limiting fuel flow increases in the order 1-butene=cyclopropane < propene < 1-pentene < 2,2-dimethylpropane < isobutane < ethylene < *n*-butane.

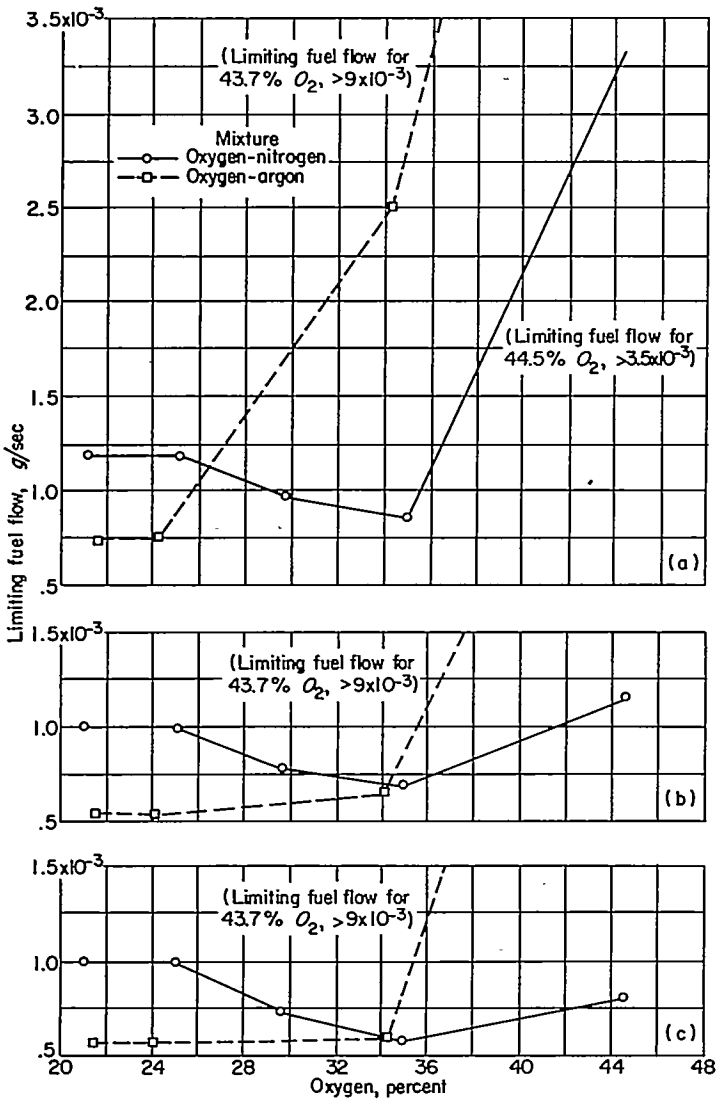
Substitution of oxygen-nitrogen mixtures for external air: Another means of making more oxygen available to the flame and thus decreasing the smoking tendency is the substitution of enriched oxygen-nitrogen mixtures for external air. Oxygen-nitrogen mixtures with oxygen concentrations ranging from 25 to 45 percent were used for this purpose. When tests were attempted at higher oxygen concentrations, two experimental difficulties were encountered. One of these difficulties was the rapid formation of solid carbon on the port of the burner tube when certain fuels were burned in an environment of 50 percent oxygen or greater, as shown in figure 10. This carbon formation eventually chokes off the flame. A similar observation was made by Parker and Wolfhard (ref. 4) while burning acetylene in pure oxygen. A second difficulty was that the point of incipient smoking was ill-defined at higher oxygen concentrations, because smoke issued from a sheath of flame rather than from a flame tip (see fig. 11). Furthermore, this smoke is light in color and much harder to detect than the heavy black smoke issuing from flames burning in air. For those flames where the accuracy in detecting the smoke point was very poor, the fuel-flow rates are only reported as being greater than a certain value.

The results of the oxygen-enrichment tests with the same eight hydrocarbons are illustrated by the solid curves in figures 12 (a) and (b) for 1-butene and 2,2-dimethylpropane, respectively. Cyclopropane and propene give curves quite similar to the 1-butene curves, whereas the remaining four hydrocarbons show behavior similar to 2,2-dimethylpropane. With the initial increase in the flow rate of a given oxygen-enriched mixture, the maximum smoke-free fuel flow also increased. The fuel flow, however, reaches a limiting value that is usually greater than that for air, although for some fuels the fuel-flow limit with oxygen-enrichment is actually less than for air.

The variations of the limiting fuel flow with oxygen-enrichment for six of the hydrocarbons are shown by the solid curves in figure 13. For propene, cyclopropane, and 1-butene, the limiting fuel flow is the same for 21 and 25 percent oxygen, but decreases for 30 and 35 percent oxygen mixtures. An increase is again observed for the 45 percent concentration. For isobutane, 2,2-dimethylpropane, and 1-pentene, the limiting fuel flow continually increases with increasing oxygen-enrichment. This increase also occurred for ethylene and *n*-butane (not shown).

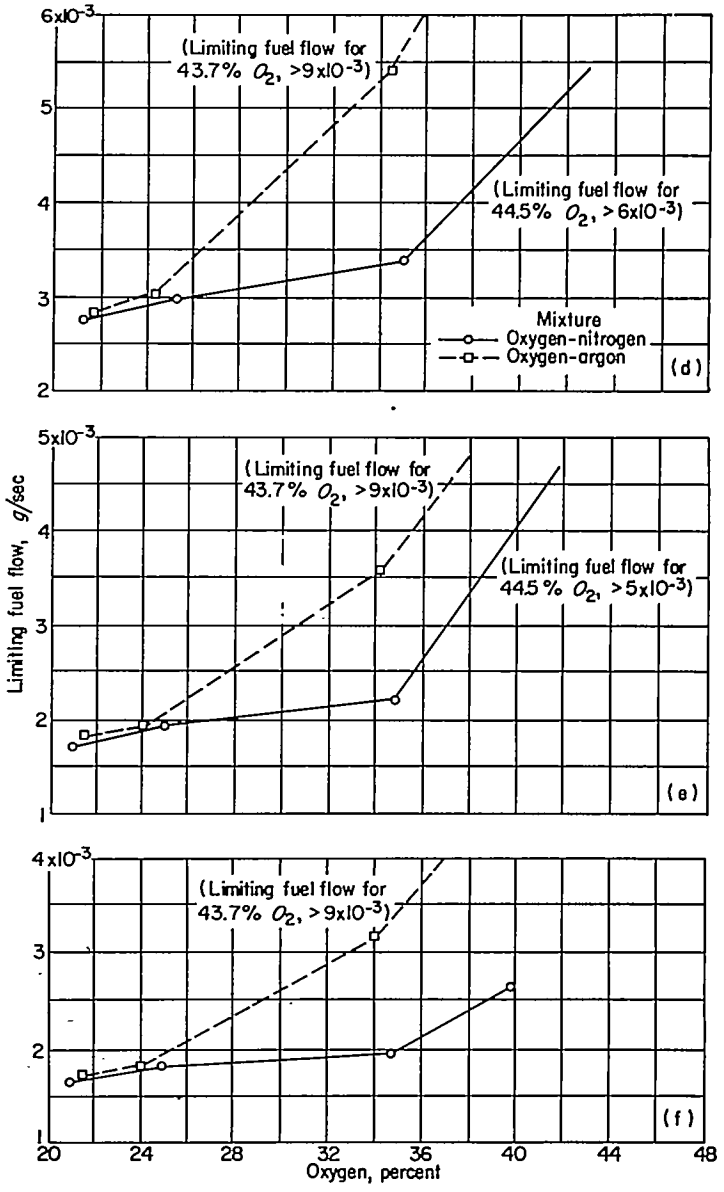
Substitution of oxygen-argon mixtures for external air: Since the oxygen-enrichment discussed heretofore not only increased the supply of oxygen reaching the flame by diffusion, but also increased the flame temperature, an attempt was made to separate the diffusion and flame-temperature effects by substituting argon for nitrogen in oxygen-enriched mixtures. (Calculations suggest that the substitution of argon for nitrogen will increase the flame temperature.)

Substituting argon for nitrogen in the oxygen-enriched mixtures caused the smoke-free fuel flow to increase except for 1-butene, cyclopropane, and propene, where, at the lower oxygen concentration, the smoke-free rates were lower than with the corresponding oxygen-nitrogen mixtures. These results are shown by the dashed curves in figures 12 and 13.



(a) Propene.
(b) Cyclopropane.
(c) 1-Butene.

FIGURE 13.—Variation of limiting fuel flow with oxygen-enrichment.



(d) Isobutane.
(e) 2,2-Dimethylpropane.
(f) 1-Pentene.

FIGURE 13.—Concluded. Variation of limiting fuel flow with oxygen-enrichment.

The results of the oxygen-enrichment and argon-substitution studies show that, when fuels of high smoking tendency (1-butene, propene, and cyclopropane) are subjected to oxygen-enrichment and consequently to increased flame temperatures or to increased flame temperatures through the substitution of argon for nitrogen, the smoking tendency increases up to a certain point. The higher flame temperatures probably promote dehydrogenation reactions relative to the breaking of carbon-carbon bonds. As was shown in the preceding section, this relative rate is probably an important factor in initiating smoke-forming steps. Therefore, it would appear that in these cases the increase in the rate of diffusion of oxygen resulting from oxygen-enrichment is less effective than the increase in dehydrogenation reactions. However, at the highest oxygen concentration (44.5 percent), the temperature may become so high that the thermal and oxidative dehydrogenation processes are no longer favored over the breaking of carbon bonds. Alternatively, at high oxygen concentrations the direct reaction of oxygen with potential carbon-forming intermediates may be favored.

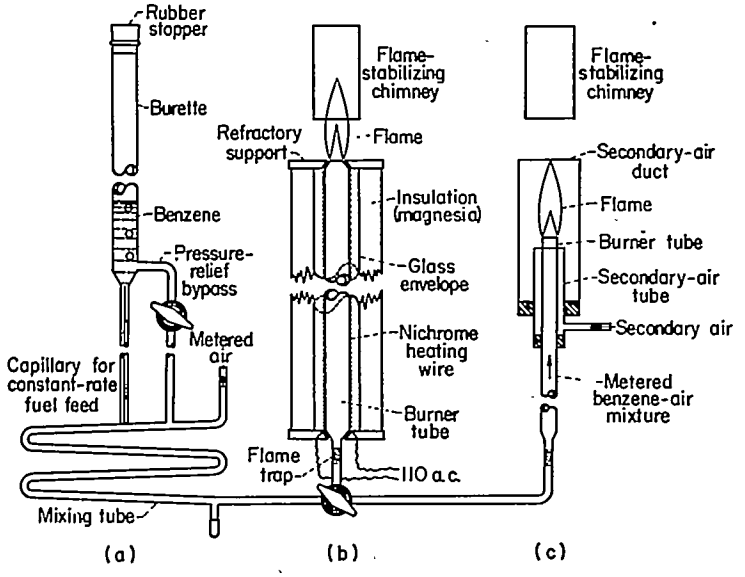
For compounds of lower smoking tendency, the smoke-free fuel flow increases with increased oxygen-enrichment for both oxygen-nitrogen and oxygen-argon mixtures. While these compounds of lower smoking tendency also undergo increased thermal decomposition at higher temperature, the decomposition may become more evenly distributed among C–C and C–H bond-breaking reactions. Actually, the breaking of single-bonded carbon atoms probably exceeds that of the C–H bonds, since, as mentioned, the C–H bonds are the stronger. Since the unsaturated carbon-carbon bonds are appreciably stronger, the carbon atoms joined by such bonds are more readily dehydrogenated and are more likely to form smoke.

Premixed flames.—Whereas in diffusion flames only the air surrounding the flames need be considered, in premixed flames the air mixed with the fuel also affects the smoking tendency. As mentioned previously, the same smoking-tendency relations were found for hydrocarbon-air flames as were found for diffusion flames (ref. 13). Flames of the greatest smoking tendency, such as the aromatics and dicyclic compounds, began to smoke at fuel-air ratios slightly richer than stoichiometric. The smoke formation, as measured by the percentage of light absorbed, varied linearly with fuel-air ratio for the fuels tested; but the effect of secondary air was not studied.

For this report, the influence of secondary-air supply on smoke formation in premixed flames was investigated with rich benzene-air flames. An apparatus for making gaseous mixtures of benzene and air is shown in figure 14 (a). Liquid benzene was dripped at a constant rate from a capillary tube into an inclined evaporating and mixing tube of borosilicate glass. Metered air was introduced into the upper end of the evaporating tube, and all the benzene evaporated into the air stream before the liquid reached the bottom of the mixing tube. Different fuel-flow rates were obtained by using capillary tubes of different lengths. All fuel and air flows were accurate to ±3.0 percent.

The formation of the first free carbon was evidenced by the appearance of the yellow pip at the tip of the inner cone, and the smoking point was evidenced by the appearance of a smoke filament at the tip of the outer mantle of the flame (fig. 15). It was felt that the effect of external physical factors would be reflected in the variation of the fuel-air ratios corresponding to these carbon-forming and smoking points.

The burner shown in figure 14 (b) was used to study the effects of secondary-air flow changes resulting from chimney changes. Increasing the chimney length from 12 to 50 centimeters causes a reduction in smoking tendency (fig. 16 (a)). Changes in the diameter (fig. 16 (a)) and position of the chimney (fig. 16 (b)) give varied results that depend on the convection in the chimney. In general, all chimney variables that reduce smoke formation do so by generating a flue effect that tends to flow more air around the flame.



(a) Benzene-air mixer. (b) High-temperature burner. (c) Ducted burner.

FIGURE 14.—Apparatus for generating and burning benzene-air mixtures.

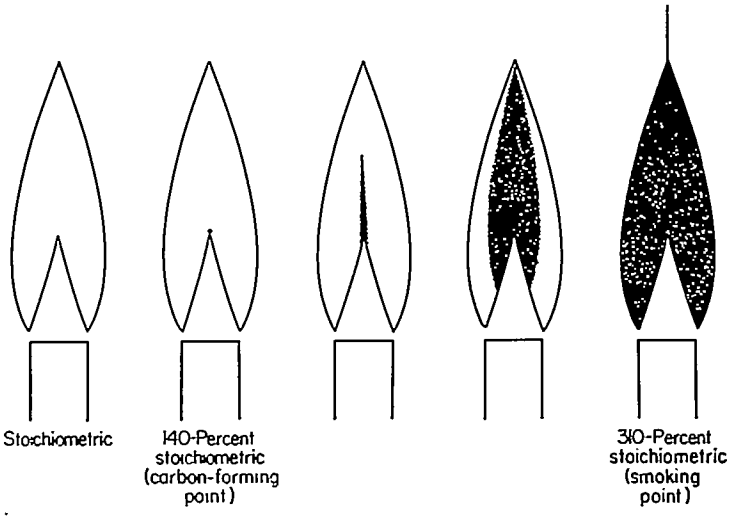
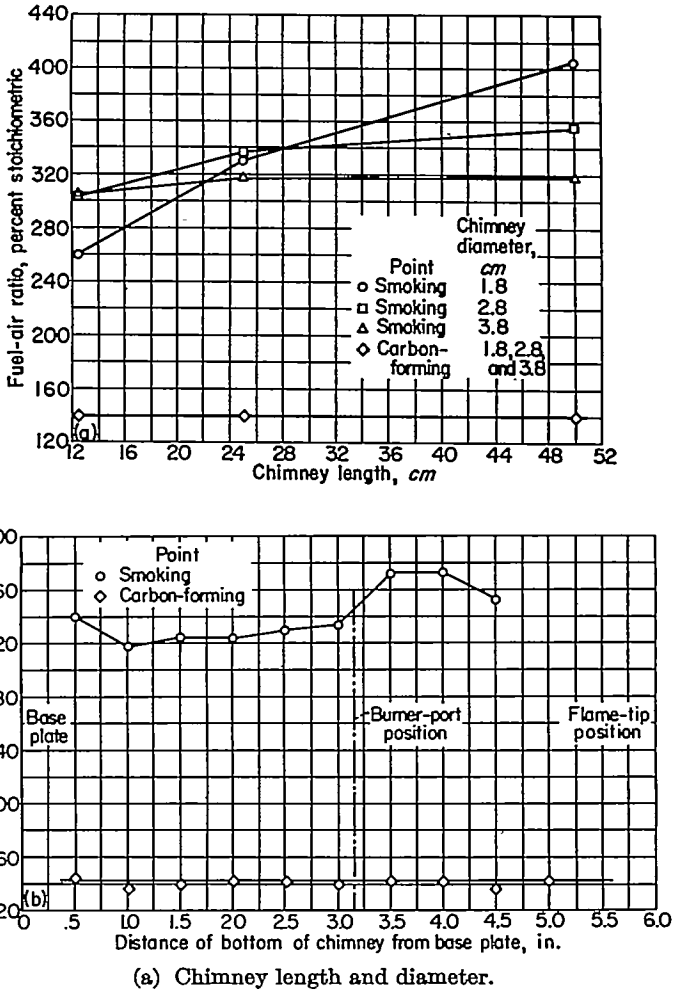


FIGURE 15.—Diagrammatic sketches of benzene-air flames. Shaded areas indicate incandescent carbon.



(a) Chimney length and diameter.

(b) Chimney-base position for 2.8- by 25-centimeter chimney.

FIGURE 16.—Influence of chimney size and position on carbon-forming and smoking points of benzene-air flames.

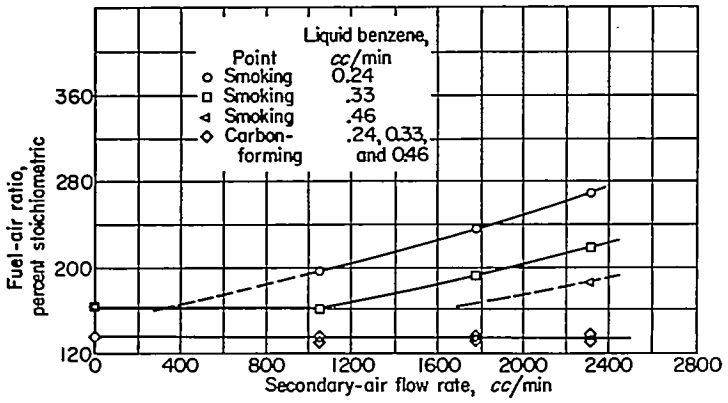


FIGURE 17.—Influence of secondary-air flow rate on carbon-forming and smoking points of benzene-air flames. Burner-tube diameter, 0.6 centimeter.

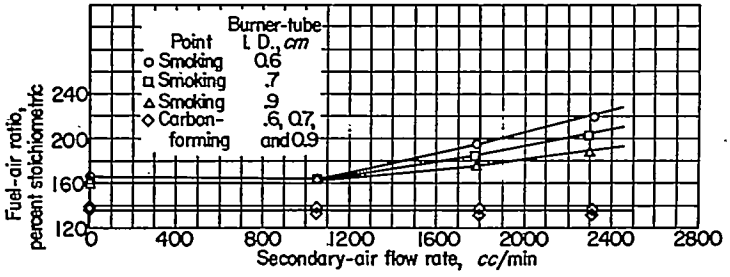


FIGURE 18.—Effect of burner-tube diameter on carbon-forming and smoking points of benzene-air flames. Liquid-benzene flow, 0.33 centimeter per minute.

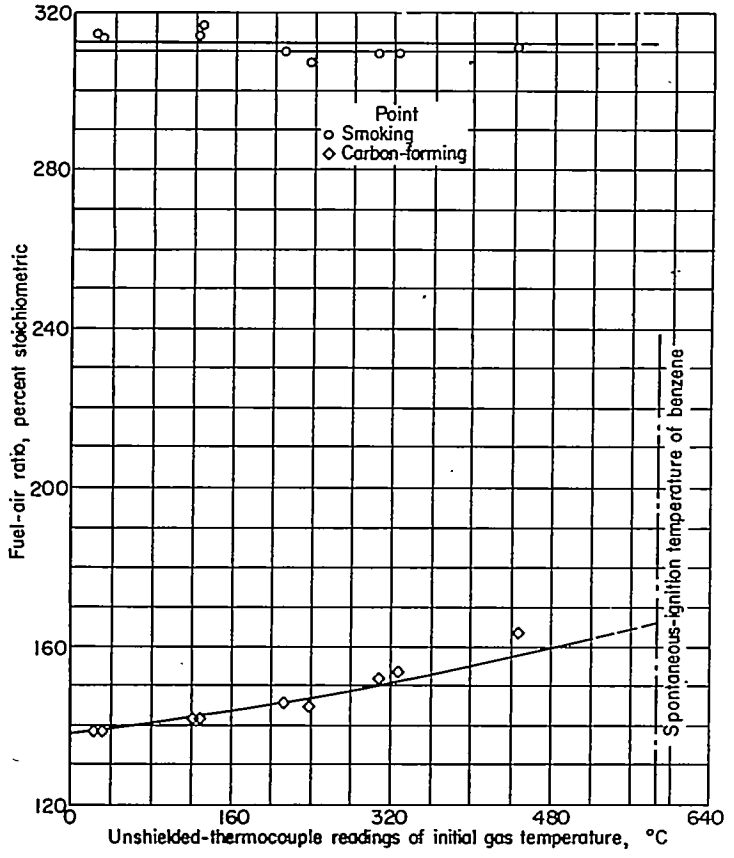


FIGURE 19.—Variation with temperature of fuel-air ratio at carbon-forming and smoking points of benzene-air flames.

The ducted burner shown in figure 14 (c) was used to study the influence of secondary air on the smoking characteristics of the benzene-air flame. With this apparatus the amount of air surrounding the flame can be controlled, as in the case of the diffusion flames discussed previously. Changes in the secondary-air flow rate or the benzene flow rate have no effect on the carbon-forming point of the flame (fig. 17). The inner cone of a slightly rich Bunsen flame seems to be isolated from air-diffusion effects. In the range of secondary-air flow rates shown in the figure, the smoking point occurs at increasingly leaner fuel-air ratios as the secondary-air flow rate is decreased. As the flame becomes richer and reaches its smoking point, however, it becomes similar to a pure diffusion flame. Thus, as for the pure diffusion flames, in the range of higher values of laminar secondary-air flow (beyond the scale on fig. 17), the variation in the secondary-air flow has no appreciable effect on the smoking-point fuel-air ratio. It remains substantially the value for a flame burning in open air with a protective chimney.

Figure 18 shows that at high secondary-air flow rates the smoking tendency is slightly reduced as the burner-tube diameter is decreased from 0.9 to 0.6 centimeter. The outer cone of the flame on the largest burner was stubbier and thicker than those on the smaller burners. A thicker cone probably inhibits diffusion and results in increased smoke formation.

The absence of secondary oxygen (either no secondary-air flows or external nitrogen flow) produces no changes in benzene-air flames up to a fuel-air ratio of 140 percent of stoichiometric. From 140 to 164 percent of stoichiometric, incandescent carbon filled the upper portion of the flame as a faint haze, but no smoke left the outer mantle. At 164 percent of stoichiometric, the flame just began to smoke, but it also became unstable and was shortly extinguished. Apparently, the incandescent carbon forming in the region of 140 to 160 percent of stoichiometric reacts farther up in the flame with the oxygen that has preferentially diffused out of the flame tip, for the flame does not smoke, even though incandescent yellow carbon is visible in the outer cone.

FUEL OR PRIMARY MIXTURE TEMPERATURE

Diffusion flames.—The apparatus shown in figure 8 (c) was used to study the effect of preheating a fuel. The same eight hydrocarbons used in the oxygen-supply experiments were employed. A 9-millimeter burner tube 700 millimeters long was jacketed by an electric heating coil. To stabilize the flame, a chimney was placed with the bottom edge level with the port of the burner tube. The maximum rate of fuel that could be burned without smoking was measured at several temperatures. The results show that preheating the fuels over a range from 30° to 190° C has no effect on smoke formation. The change in flame temperature obtained by this method is less than 1 percent.

Premixed flames.—In reference 14, the appearance of yellow incandescent carbon in the flame was used to measure the effect of temperature on propane, propene, benzene, and kerosene flames. Over a temperature range from —40° to 500° C, the appearance of incandescent carbon in the flame occurred at slightly higher fuel-air ratios as the temperature was increased.

The effect of the initial temperature was studied further for benzene-air mixtures with the apparatus shown in figures 14 (a) and (b). The carbon-forming point and the smoking point were measured at a series of temperatures ranging from room temperature to 450° C. The gas temperature was measured before and after each test by inserting a thermocouple 5 centimeters into the top of the burner tube. Figure 19 shows that, as the initial temperature of the gas mixture is raised from room temperature to 450° C, the smoking-point fuel-air ratio remains unchanged, but the carbon-forming-point fuel-air ratio increases from 140 to over 160 percent of stoichiometric.

The Bunsen cone generates a sheath of hot gaseous combustion products through which oxygen from the surrounding air must diffuse in order to react with the incandescent carbon. Those variables which increase the diffusion of oxygen through this zone should improve the smoke-burning characteristics of the flame. The rise in initial gas-mixture temperature caused no change in the smoking point.

It is probable that the enhanced diffusion rate due to the hotter gases was compensated for by the greater diffusion path length resulting from increased gas expansion. The variation of the carbon-forming point with temperature might be explained on the basis of preferential diffusion. At room temperature, the lighter oxygen and nitrogen molecules diffuse away from the heavier hydrocarbon molecules in the rounded flame tip (ref. 15, pp. 277–278). At higher initial gas temperatures, pyrolysis of the hydrocarbons to two- or three-carbon-atom chain fragments is enhanced, and it might be expected that the diffusion rates of all particles become comparable. In this case the fuel-air ratio in the tip of the flame would remain the same as that in the bulk of the premixed gas. As a result, the carbon-forming point at high initial temperatures would be the same as the smoking point with no secondary-air flow (figs. 17 and 19). Since temperature influenced the carbon-forming point, but, as previously indicated, secondary-air flow did not, it appears that no appreciable amount of external oxygen was able to diffuse into the flame tip.

FUEL-FLOW RATE IN PREMIXED FLAMES

Using the benzene-air apparatus previously described, the rate of the benzene flow was varied and the air-flow rate was adjusted until a smoking-point and a carbon-forming-point fuel-air ratio were determined for each benzene flow rate. This experiment was conducted at room temperature and at 450° C. The flame length at the smoking point was also measured at each benzene flow rate. The results are shown in figure 20. As the benzene flow rate was increased, the flame length increased linearly, the smoking-point fuel-air ratio decreased in some exponential fashion, and the carbon-forming fuel-air ratio remained constant. If it is assumed that the unit-volume concentration of carbon to be burned was the same in these flames of different fuel-flow rates, the geometry of the flame might be responsible for the increased smoking tendency of the longer flames. As a cone with constant-diameter base increases in length, its surface-to-volume ratio decreases. Since less surface in proportion to the volume of reactants is available in the longer

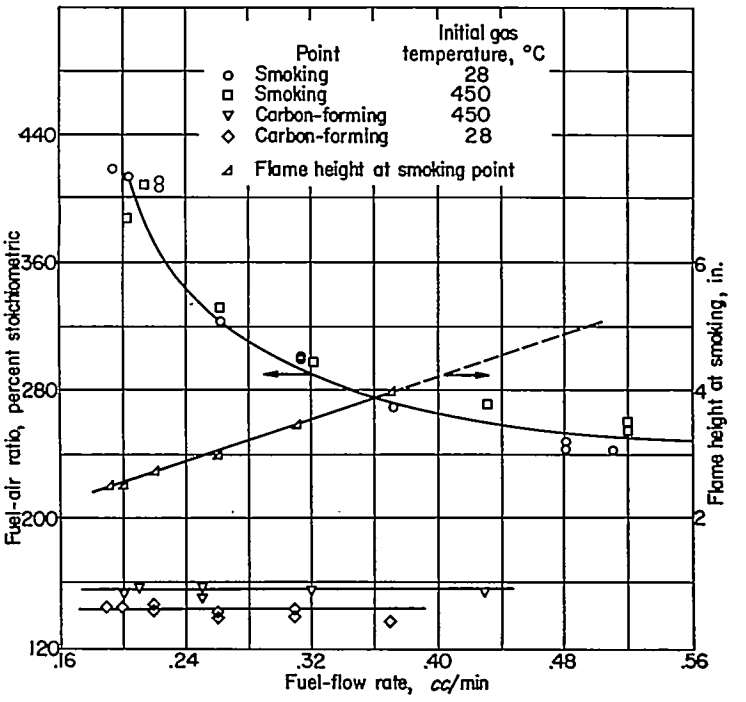


FIGURE 20.—Variation of flame height and fuel-air ratio with fuel-flow rate at carbon-forming and smoking points of benzene-air flames.

flames, less secondary oxygen diffuses into the outer cone, and the smoking-point fuel-air ratio decreases.

PRESSURE

Diffusion flames.—The effect of pressure on smoke formation was investigated by burning nine hydrocarbon fuels as diffusion flames in a pressure chamber. A sketch of the apparatus used to study the effect of pressure from ¼ to 4 atmospheres on smoke formation is shown in figure 21.

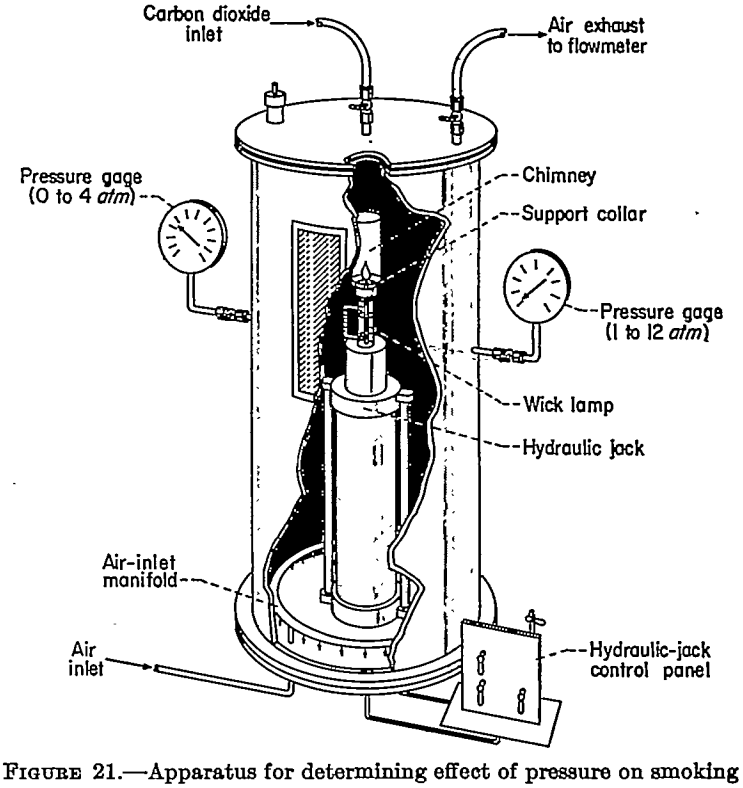
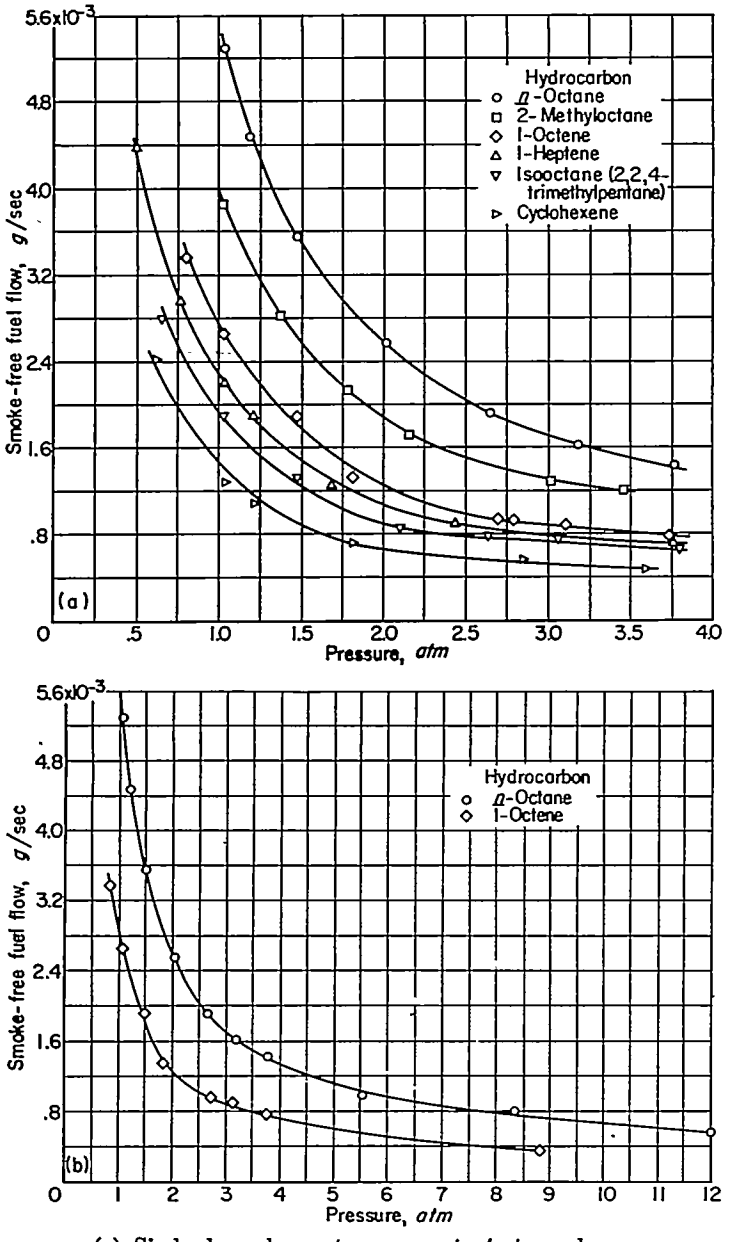


FIGURE 21.—Apparatus for determining effect of pressure on smoking tendency.

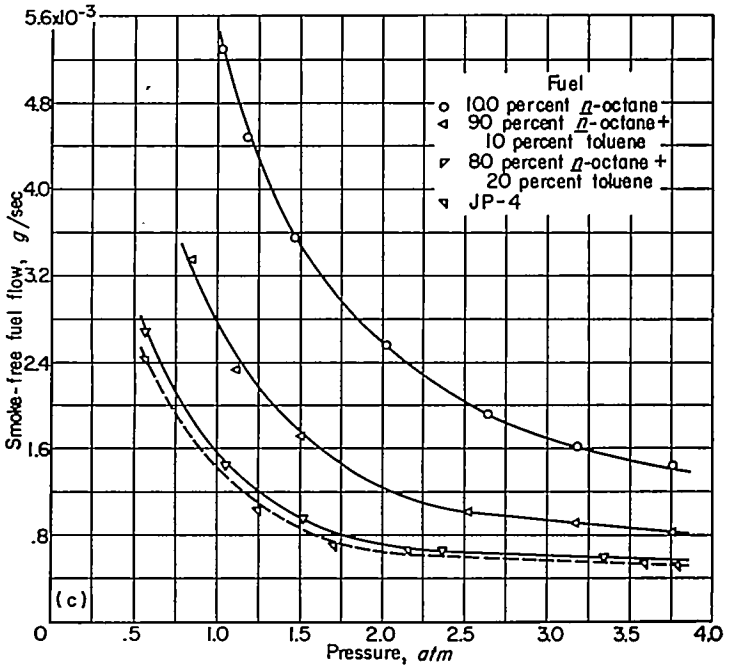
The pressure chamber was approximately 300 millimeters in diameter and 700 millimeters high. To obtain pressures above atmospheric, compressed air was admitted at the bottom of the chamber and combustion products were removed from the top at a rate of 220 cubic centimeters per second. Appreciable variations could be made in the exhaust rate without changing the smoking tendency of the flame. Pressures below 1 atmosphere were obtained by connecting a vacuum line to the top of the chamber; in this case the inlet air was metered. Carbon dioxide could be admitted through the top of the chamber to extinguish the flame. The fuels were burned from a wick lamp with a calibrated side arm. The level of the lamp, the height of the wick above a supporting collar, and thus the fuel rate, were controlled. Both the fuel level in the wick-lamp side arm and the smoking point were observed through a Lucite window. Reproducibility of the fuel-flow rate was approximately ±3 percent.



(a) Six hydrocarbons at pressures to 4 atmospheres.

(b) Two hydrocarbons at pressures to 12 atmospheres.

FIGURE 22.—Variation of smoke-free fuel flow with pressure.



(c) Various fuels and blends at pressures to 4 atmospheres.

FIGURE 22.—Concluded. Variation of smoke-free fuel flow with pressure.

In figure 22 (a) the maximum rate at which six pure hydrocarbon compounds (*n*-octane, 2-methyloctane, 1-octene, 1-heptene, isooctane, and cyclohexene) could be burned smoke-free is plotted against pressure over a range of about ½ to 4 atmospheres. For *n*-octane and 1-octene, the pressure range was extended as shown in figure 22 (b). In figure 22 (c) the maximum rate for 100 percent *n*-octane, two blends of *n*-octane and toluene, and a JP–4 fuel are plotted against pressure. As can be observed from figure 22, the rate at which the fuels can be burned smoke-free decreases consistently with increasing pressure. The JP–4 fuel and the two blends of *n*-octane and toluene show the same variation in smoke formation with pressure as do the pure hydrocarbon compounds.

In order to study the effect of pressure in the range 4 to 20 atmospheres on ethane and ethylene flames, the pressure chamber was modified and the fuels were burned from a 2-millimeter-inside-diameter tube. In this case the fuel rate was not measured, but the maximum flame height at which the fuels could be burned without producing smoke was used as a measure of smoking tendency. (It is generally known that the height of a diffusion flame is proportional to the fuel-flow rate (ref. 15, p. 534).) Figure 23 shows that the maximum flame height decreased with increasing pressure over the entire range.

Plots of the smoke-free fuel flow (flame height) against the reciprocal of pressure are shown in figures 24 and 25. The straight lines obtained in these plots indicate that the change in smoke-free fuel flow is inversely proportional to the pressure. The rate of diffusion, and consequently the rate of mixing of fuel and air, may therefore account for the variation of smoke formation with pressure.

Premixed flames.—In a spectroscopic study of a premixed ethylene flame (ref. 16), it was observed that smoke formation started to occur as the pressure was increased. However,

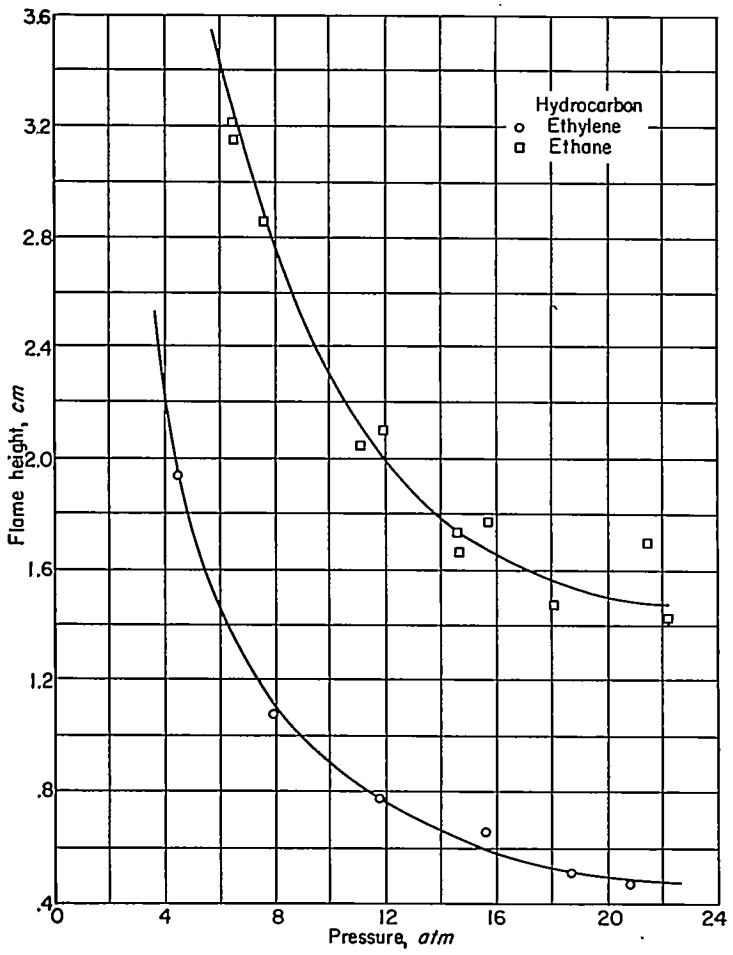
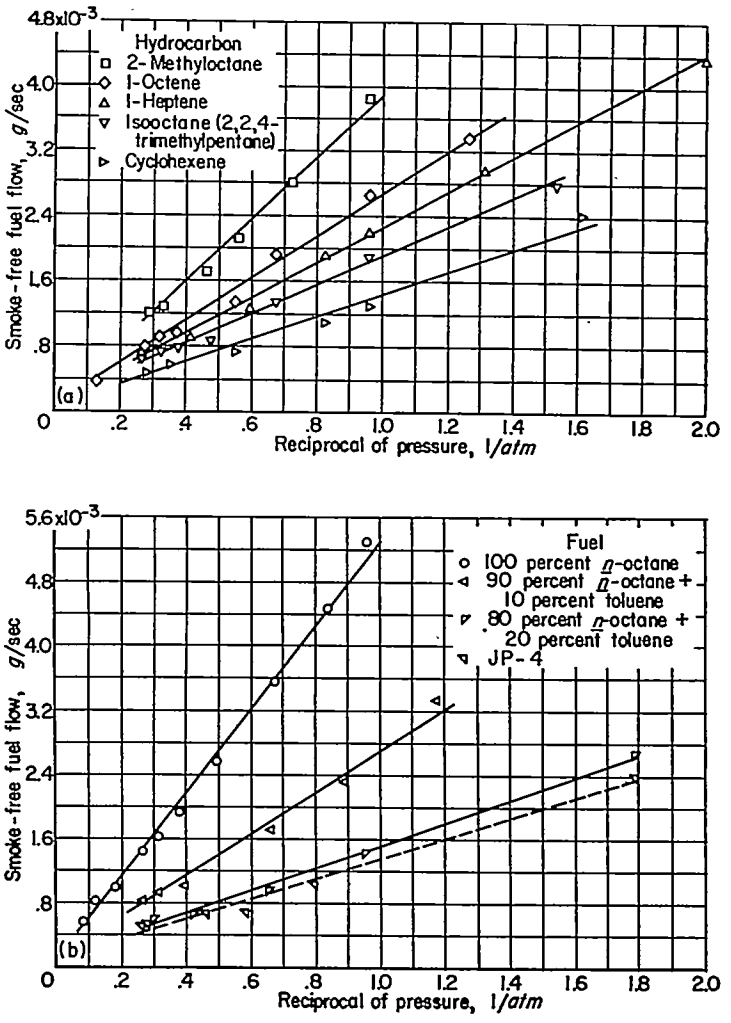


FIGURE 23.—Variation of flame height at smoking point with pressure. Flame height proportional to fuel flow.



(a) Five hydrocarbon fuels.
(b) Various fuels and blends.

FIGURE 24.—Variation of smoke-free fuel flow with reciprocal of pressure.

from a study of the formation of smoke from an acetylene-oxygen flame at various pressures (ref. 17), it was concluded that the effect of pressure on smoke formation from Bunsen flames is probably slight. The effects observed in reference 16 were attributed in reference 17 to changes in experimental parameters such as mass flow and to the influence of the burner wall. The results from the diffusion-flame study reported herein suggest that the increase in smoke formation with pressure results from decreases in diffusion rates; it seems reasonable, therefore, that smoke formation from a Bunsen flame that contains all its oxygen should be independent of pressure.

POSTULATED MECHANISM OF SMOKE FORMATION

DIFFUSION FLAMES

In the preceding sections it was proposed that the relative ease of removal of hydrogen atoms from the molecule as compared with the breaking of carbon bonds is responsible for the variations in smoking among different fuel types burning as diffusion flames. This proposal, along with the oxygen-supply studies, indicates that the thermal and oxidative dehydrogenation processes, which occur very early in the burning process, influence the further course of smoke formation. The thermal dehydrogenation probably occurs as soon as the fuel enters a laminar diffusion flame, because the fuel is heated to temperatures of the order of 800° C or higher before coming in contact with oxygen.

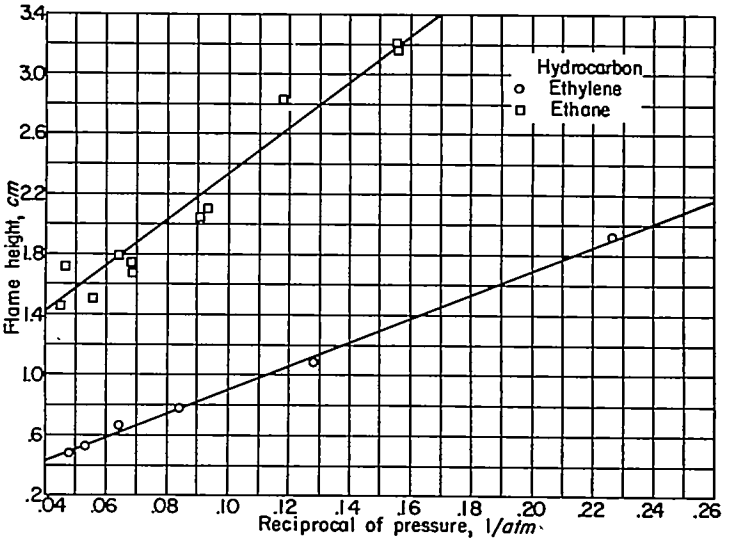


FIGURE 25.—Variation of flame height at smoking point with reciprocal of pressure. Flame height proportional to fuel flow.

Other investigators who have considered the importance of dehydrogenation reactions tend to support this proposal. For example, the energy requirements for removal of a hydrogen atom from an acetylene molecule by a free hydrogen atom,

$$H+C_2H_2 \rightarrow H_2+C_2H$$

were considered in reference 18. This reaction has an activation energy of only 5 kilocalories per mole, which indicates that it could easily occur. Activation energies for the reaction of hydrogen atoms with various other hydrocarbon compounds are of similar magnitude (ref. 18).

It was observed in reference 19 that suppression of the hydrogen-atom concentration in flames accompanies the suppression of smoke formation. Thus, smoke formation could be prevented by reactions that consume hydrogen atoms or render them ineffective. Reference 20 suggests that smoke formation could be suppressed by carbon monoxide and nitrogen, which serve as nuclei for the recombination and removal of hydrogen atoms. Reference 21 reports that, in addition to hydrogen atoms, other atoms and radicals such as those found in the pyrolysis of halogen compounds also increase smoke formation. All these active species probably promote polymerization reactions leading to smoke by stripping hydrogen from the fuel molecules. Even if halogen atoms react with and remove some of the hydrogen atoms, the concentration of fuel molecules is so much greater than the concentration of the short-lived hydrogen atoms that the dehydrogenation process predominates. It is therefore proposed that the removal of hydrogen atoms from the fuel molecules both by thermal processes and by active atoms is probably the initial process involved in the formation of smoke.

The steps that might occur after total or partial dehydrogenation are controversial. Since aromatics have the greatest smoking tendencies, and since the graphite structure of carbon particles resembles the molecular structure of the multiringed homologs of benzene, the formation of smoke by a build-up of aromatic ring structures has been suggested. This theory is not opposed to the initial step of hydrogen removal, since the fuels would have to lose some hydrogen atoms before a polymerization of the rings might begin. However, absorption spectroscopic examinations of a benzene flame in the ultraviolet region (ref. 4) indicate that benzene is consumed in the lowest portion of the flame and that an appreciable gap exists between the disappearance of benzene and the appearance of smoke particles. No intermediate aromatic products, which should be readily detectable in the ultraviolet, are found in this region. The absence of aromatic intermediates in this gap is evidence against the ring-building theory.

Thorp, Long, and Garner (ref. 22) analyzed the smoke from a flat benzene flame and found diphenyl to be present, thus supporting the aromatic-ring-building theory; but in later work (ref. 23) they did not find diphenyl present in the products of the soots from paraffinic or naphthenic fuels. Consequently, it is unlikely that carbon formation in hydrocarbon diffusion flames occurs through diphenyl, the polyphenyls, or the polycyclic aromatics as intermediate compounds (ref. 23).

Parker and Wolfhard (ref. 4) reject the aromatic-ring-building theory; but they have proposed as mechanisms for smoke formation (1) the formation of large molecules that may graphitize from within, or (2) an increase in the concentration of moderately high molecular weight hydrocarbons until the saturation vapor pressure is reached, at which time condensation occurs to form a mist of droplets that form nuclei and graphitize. Observations on the physical nature of smoke (ref. 24) show that the first mechanism is improbable. Frazee and Anderson (ref. 18) object to both mechanisms, on the basis of prohibitive energy requirements and other considerations. Porter (ref. 25) concludes from considerations based on the time available for polymerization and on the nature of the smoke formed that the droplet-formation mechanism or polymerization mechanisms in general do not contribute to smoke formation to any significant extent in ordinary diffusion flames.

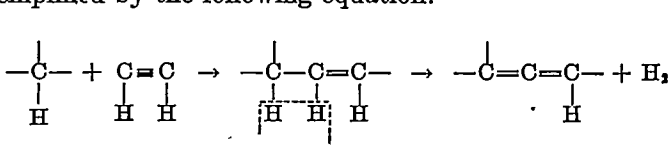
Porter (ref. 25) believes, instead, that fuels in combustion waves first decompose to form lower molecular weight hydrocarbons such as acetylene as a result of both thermal decomposition and partial oxidation. By rapid adiabatic photolysis he obtained rates of liberation of heat and active particles in a reaction vessel comparable to those which occur in flames. A rapid quenching resulted in the retention of a fraction of all stable intermediates. Complete analysis of the products showed no higher hydrocarbons. Porter therefore proposes a series of reactions:

$$C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow \text{carbon}$$

Previously, Tropsch and Egloff (ref. 26) showed that acetylene is a product of the pyrolysis of pure hydrocarbons. They passed ethane rapidly through a heated tube for various contact times and found that ethylene, acetylene, and carbon were formed. This experiment simulates the reactions that might occur in the lowest portion of a diffusion flame where the fuel is heated before coming into contact with oxygen.

Since acetylene may be the last stable product to appear before smoke formation, the final step in the mechanism of smoke formation would be that leading from acetylene to smoke. If all hydrogen atoms were removed from the C_2H_2 molecule, the mechanism for the final step in the formation of smoke would be that of the polymerization of C_2 radicals. Such a mechanism was at one time considered a plausible and promising explanation of smoke formation (e. g., ref. 16). However, the theory of smoke formation via C_2 has now been rejected by numerous authors (refs. 4, 18, and 25).

A mechanism based on simultaneous polymerization and dehydrogenation is proposed in reference 25 to account for the steps between acetylene and smoke. The reaction is exemplified by the following equation:



Transient diene structures like those indicated were also deemed important in reference 23.

Analogous to the work of reference 25 is the indication in reference 18 that a mechanism involving free radicals or atoms is important in the formation of smoke. The activation-energy requirements for such free-radical reactions were considered, and the following values were reported:

	Energy, kcal/mole
$C_2H+C_2H_2\rightarrow C_4H_3\rightarrow C_4H+H_2$	~58
$C_2H+C_2H_2\rightarrow C_4H_2+H$	~29
$C_2H_2+C_2H_2\rightarrow C_4H_3+H$	~60

Reference 18 indicates that the first equation is of the type suggested by Porter and proposes that, while the reaction is feasible and may occur to some extent, its activation energy is much higher than that for the reaction shown in the second equation. The third equation shows a possibility for the use of the energy of combination in initiating reactions perhaps more effectively than by purely thermal means. At particularly high temperatures, more than one reactive radical or hydrogen atom could result from a step such as the second equation, and chain-branching might result. Steps such as these can occur with molecules containing larger and larger numbers of carbon atoms, leading eventually to formation of carbon nuclei and even to growth of a particle.

In summary, the general mechanism of smoke formation, based on the information currently available, probably proceeds as follows:

(1) Some hydrogen atoms are removed from the fuel molecule by thermal processes. The hydrogen atoms, in turn, cause further dehydrogenation of the molecule. The more readily the hydrogen atoms are removed as compared with the breaking of carbon bonds, the greater is the probability of smoke formation.

(2) After these initial dehydrogenation steps, the fuel molecules probably continue to decompose to smaller molecules and fragments of molecules. Acetylene is reported to be the last stable product to appear before smoke formation. Various authors have shown that a breakdown to smaller products must occur rather than an immediate growth to polymers or aromatic ring structures.

(3) Although a breakdown to small fragments and relatively small molecules takes place, the formation of smoke through polymerization of C_2 radicals has been rejected. It has been proposed that in the final stages the small molecules such as acetylene and hydrocarbon fragments undergo a simultaneous polymerization and dehydrogenation to form smoke.

PREMIXED FLAMES

When a premixed flame is made increasingly richer, a point is reached at which a yellow tip appears on the flame. If the air supply is reduced still further, the yellow tip increases in size until the whole flame is luminous. As the air flow approaches zero, the flames usually smoke. A gradual transition from a premixed flame to a diffusion flame can be obtained with no discontinuity in the process.

The oxidation and the pyrolysis processes probably occur in both types of flame. In the premixed flames, oxidation processes probably predominate over those of pyrolysis and polymerization. As the flames become richer, pyrolysis and polymerization probably predominate and submerge the oxidation reactions. The oxidation processes need go only as far as carbon monoxide to prevent luminous carbon formation in the flame. Thus, flames appreciably richer than stoichiometric need not produce luminous carbon even though an oxygen deficiency exists.

Apparently, when luminous carbon does appear in the flame, it occurs in those regions devoid of oxygen. It is thought that lighter oxygen and nitrogen molecules diffuse preferentially out of the top of the flame. The tip would thus contain a relatively higher concentration of fuel and would be the first location to be depleted of oxygen. If carbon formation does occur in the absence of oxygen, there is good reason to believe that the mechanism of smoke formation is the same in both rich premixed and diffusion flames.

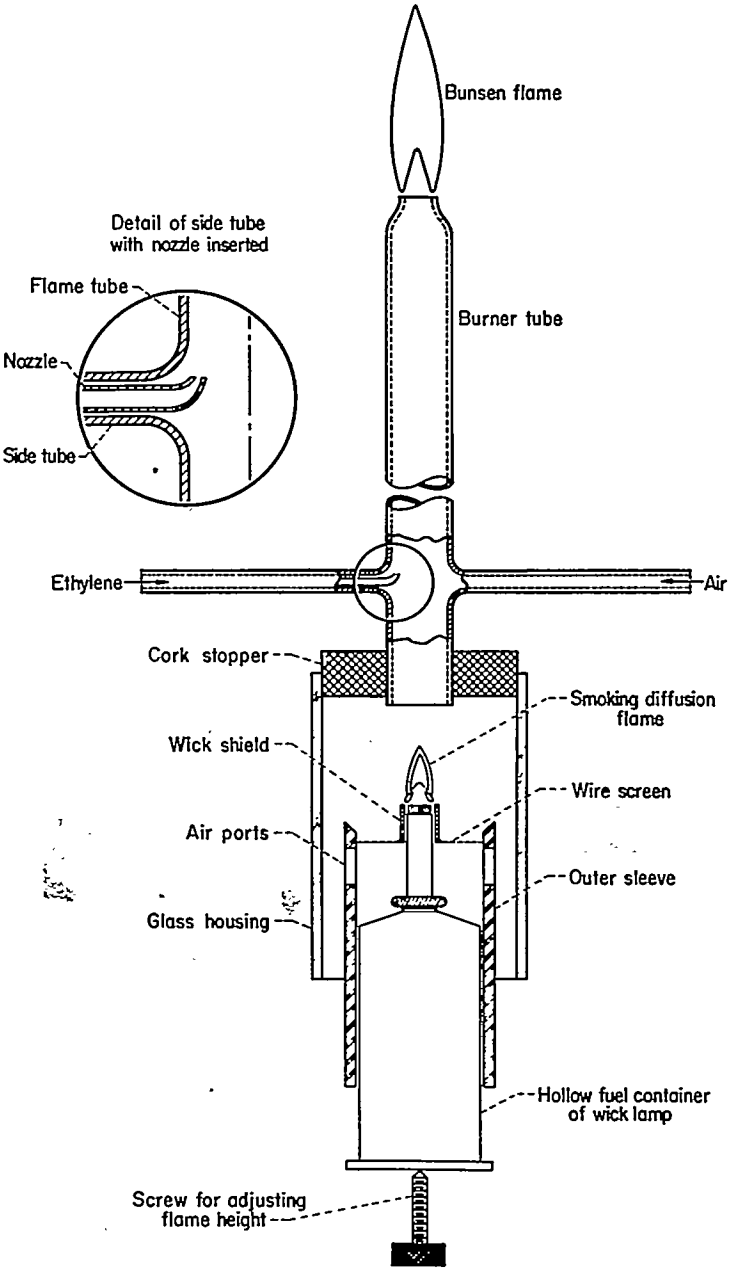


FIGURE 26.—Ethylene-air smoke burner.

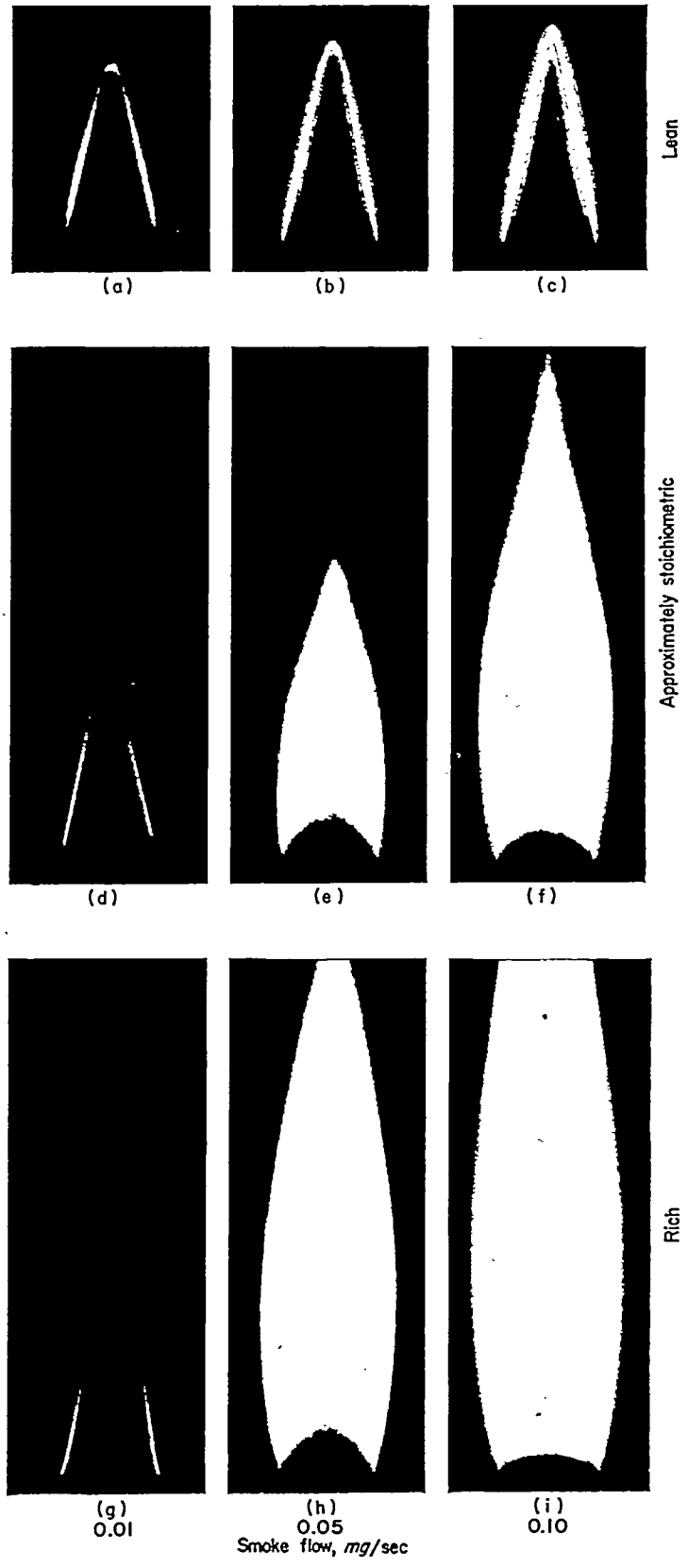


FIGURE 27.—Bunsen flames burning homogeneously admixed smoke. Ethylene flow rate, 8.0 cubic centimeters per second. X2.

COMBUSTION OF SMOKE IN FLAMES

ETHYLENE-AIR SMOKE BURNER

As shown previously, the smoke that is exhausted from turbojet combustors appears to be partially consumed in passing through the combustor. Therefore, it is of interest to determine whether a similar process could be accomplished in laboratory flames and at what rate this smoke could be consumed. This determination was made by generating smoke from a wick lamp and passing this smoke through a premixed ethylene-air flame.

The burner used for this purpose is shown in figure 26. The smoke source was a wick lamp mounted in a modified housing. The hot exhaust products generated a flue effect, which carried the smoke up the glass burner tube. Ethylene and air were introduced through the side tubes and the mixture was burned at the top of the burner tube as a Bunsen flame. The ethylene nozzle shown in the figure was used for smoke-filament burning discussed later. For homogeneously mixing smoke with fuel and air, the nozzle was removed so that the ethylene and air jets impinged on each other to give mixing. The indeterminate amount of air entering the base of the tube prevented any direct measurement of the fuel-air ratios. However, the test-flame fuel-air ratio could be estimated with approximately a ± 10-percent error by comparing the color of the unknown flame with ethylene-air Bunsen flames of known fuel-air ratios. The ethylene flow rate was accurate to ± 5 percent. The amount of smoke generated per second by the smoke lamp was determined by collecting and weighing the smoke issuing from the top of the burner with no flame.

BURNING OF HOMOGENEOUSLY MIXED SMOKE

Photographs of Bunsen flames burning homogeneously mixed smoke at lean, stoichiometric, and rich fuel-air ratios are shown in figure 27. The fuel flow was 8.0 cubic centimeters per second in all cases. The smoke flow in the three vertical rows of photographs was approximately 0.01, 0.05, and 0.10 milligram per second, respectively. For a lean flame, the addition of a smoke concentration of 0.01 milligram per second (fig. 27 (a)) caused a faint aureole to appear around the inner cone. With a rich flame (fig. 27 (g)), this aureole increased in size, extending farther into the outer cone as an incandescent yellow haze. As 0.05 milligram of smoke was added to flames of each fuel-air ratio, the aureole around the inner cone brightened to the intense light yellow characteristic of hydrocarbon diffusion flames (fig. 27 (h)). Increasing the amount of smoke to 0.10 milligram per second caused the bright region to extend into the outer cone until the whole outer cone was bright with incandescent carbon (figs. 27 (c), (f), and (i)). For very lean flames, the maximum amount of smoke burns in a compact aureole (fig. 27 (c)), whereas the same amount of smoke in rich flames burns as a large brush flame around the inner cone (fig. 27 (i)). No smoke was observed to leave the tips of any of these flames.

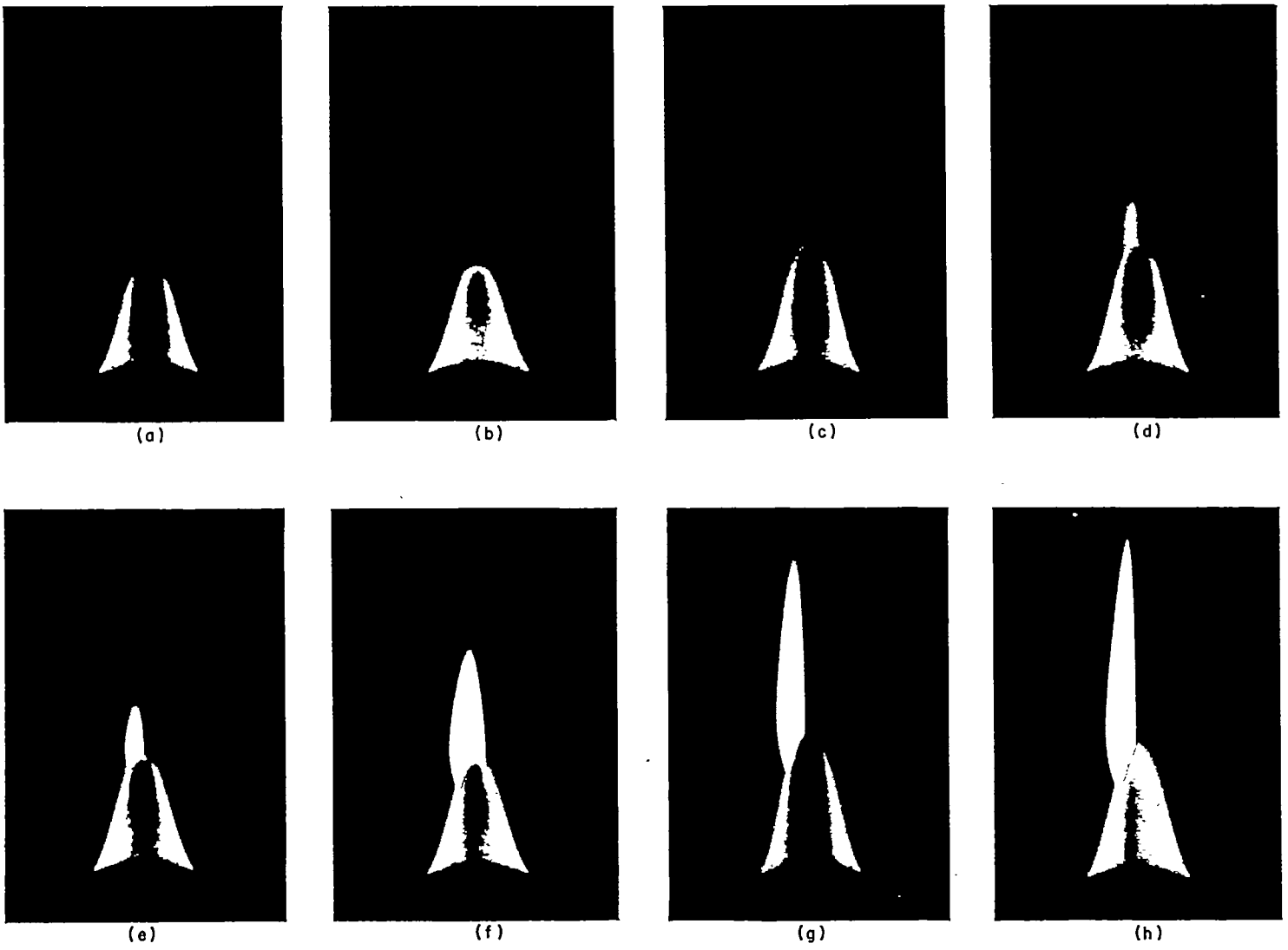


FIGURE 28.—Smoke filaments burning in ethylene-air Bunsen flames.

The amount of smoke that could be burned in the flame was limited by the operation of the smoke lamp. At smoke deliveries above 0.12 milligram per second, the smoke formed clumps, some of which passed through the ethylene flame as particles of soot. Some collection measurements made with and without a flame at a smoke-flow rate of 0.20 milligram per second indicate that 85 percent of the sooty smoke was consumed in the flame.

BURNING OF SMOKE FILAMENTS

The large percentage of smoke consumed in the fuel-soot mixtures appeared to be limited by the formation of clumps of smoke when the smoking rate of the wick lamp exceeded a critical point. To test the ability of the flame to burn higher smoke concentrations, the smoke of the wick lamp was concentrated in a narrow filament rather than spread uniformly, thus producing local high concentrations of smoke. When the ethylene nozzle shown in figure 26 was used, the smoke passed up the tube as a concentrated filament of finely divided carbon smoke to the rich Bunsen flame seated on the burner.

Figure 28 (a) shows the rich Bunsen flame generated on the nozzle when the air flow is shut off and all the air is supplied by the chimney convection due to the smoke lamp. The flow rate of ethylene in all the flames shown in figure 28 was 1.2 cubic centimeters per second. Figures 28 (b) to (h) show flames burning smoke filaments whose flow rates vary from appreciably less than 0.01 to approximately 0.07 milligram per second. With even the smallest filaments, the smoke is not completely consumed in the inner cone but extends an appreciable distance into the outer cone before it is completely burned. As the smoke concentration is increased, the incandescent streak of carbon extends higher into the outer cone until it reaches the limits of the outer cone. Any further increase beyond 0.07 milligram per second causes a thin filament of smoke to escape from the tip of the incandescent streak. Continued increases in smoke concentration increase the size of this escaping smoke filament.

At the conditions of incipient break-through of the smoke from the outer cone (fig. 28 (h)), calculations were made of the ratio of smoke carbon atoms to ethylene carbon atoms within the smoke filament. These calculations, which were based on the diameter of the filament, the diameter of the burner, and the concentration of smoke and ethylene, show a ratio of approximately 2:1 for smoke to ethylene carbon atoms. In this experiment, these high concentrations of smoke were burned in only a small fraction of the total hydrocarbon-air flame front and it is not known to what extent the remainder of the flame contributed to this process. It is unlikely that smoke would have been completely burned if equally high concentrations had been fed to all the flame front. Nevertheless, the results do indicate that relatively large amounts of smoke can be completely consumed in a flame.

MECHANISM OF SMOKE BURNING

The bright inner cone of the Bunsen flame is the reaction zone for a fuel-air mixture. Added smoke, however, tends to burn in the outer cone, even in lean flames (fig. 27 (a)). When the smoke is concentrated in a filament, even the most minute amounts also burn into the outer cone of a rich flame as a faint streak (fig. 28 (c)). The reason for this behavior may be found in the mechanism of smoke burning.

Electron-microscope examination of smoke collected from ethylene, benzene, and turbojet fuel burning as diffusion flames revealed that all three gave smoke particles of relatively uniform size, averaging from 300 to 500 angstroms in diameter. Smoke that passed through the turbojet engine varied widely in particle size from 500 angstroms in diameter down to particles too small to resolve in the microscope (fig. 2 (b)).

The different burning behavior of finely divided smoke and sooty smoke was probably due to the physical configuration of the carbon-particle chains, rather than to the carbon particles themselves. The compact soot particle would be less open to oxygen attack than would the same weight of carbon dispersed in long open chains. The finely divided smoke probably consisted of long open chains of carbon particles, whereas the coagulated smoke or soot was probably matted clumps of such carbon-particle chains.

Smoke burning may occur as follows: The carbon-particle chains are heated to incandescence in the inner cone and are kept hot in the outer cone. The smoke is in motion relative to the reaction zones and thus passes through them in a finite time. Oxygen probably reacts with the incandescent surfaces of the carbon particles to form carbon monoxide, with the result that the particles are eroded away as they pass through the flame zones. This process requires time to proceed to completion; thus, the major portion of the reaction would tend to occur in the outer cone. Oxygen must therefore exist in the outer cone to react with the hot carbon. In lean flames the oxygen is supplied both by the excess air in the mixture and by the diffusion of oxygen into the outer cone from the surrounding atmosphere. With this excess oxygen present, the carbon particles are rapidly oxidized and the luminous yellow color characteristic of hot solid carbon dies out a short distance from the inner cone. In flames richer than stoichiometric, most of the oxygen reacting with the carbon smoke must diffuse into the outer cone from the surrounding atmosphere. The longer time required for sufficient oxygen to diffuse into the outer cone to react with all the carbon present means that the smoke travels farther upward in the flame before it is completely consumed. The result is a large yellow brush flame such as the one shown in figure 27 (i).

The shape of the burning filaments shown in figure 28 is probably due to the nature of the diffusion and reaction processes. The outer layers of the hot smoke filament would be oxidized first, and the central core would therefore last longer and drift farther upward before it was finally consumed. Such behavior would result in the pointed filament streaks shown in figure 28. If the filament smoke concentration was too high, the central core would drift out of the hot reaction zone and appear as a thin filament of smoke. In similar fashion, a dense clump of soot would pass through the whole reaction zone without burning completely.

It would appear that a flame can burn relatively large amounts of carbon smoke if the smoke is finely divided and sufficient oxygen is present to react with all the carbon while it is in the hot outer cone. With flames leaner than stoichiometric, the maximum smoke-burning capacity would seem to be limited by the minimum fuel-to-smoke ratio that will still give a stable flame when enough air is added to burn all the smoke. (If the flame burns in air, part of the oxygen can be supplied by the diffusion of air into the outer cone.) With flames richer than stoichiometric, the carbon-burning capacity of the flame becomes critically dependent on the amount of air entering the outer cone. This introduction of secondary air is important in engineering applications.

SUMMARY OF RESULTS

This study of the formation and reactions of smoke may be summarized as follows:

1. Smoke consists of spherical solid particles attached to each other to form lace-like filaments. The smoke particles vary from 0.01 to 1.0 micron in diameter. In addition to the carbon, smoke contains about 5 percent of the hydrogen originally present in the hydrocarbon.

2. The rate at which a fuel can be burned without producing smoke varies with fuel type in the approximate decreasing order: n-paraffins $>$ isoparaffins $>$ cycloparaffins $\gtrsim$ olefins $>$ cycloolefins $\geq$ diolefins $\sim$ alkynes $>$ n-alkylbenzenes. For the n-paraffins, smoking tendencies increase with increasing molecular weight; this effect might be related to variations in the diffusion coefficient with molecular weight. It is postulated that, for isomers and for different fuel types of similar molecular weight, the one with the most stable carbon skeleton shows the greatest tendency to smoke.

3. Smoke-free fuel-flow rate rises to a limiting value as oxygen supplied to the flame is increased by raising external air flow.

For diffusion flames, when the oxygen content of the air is increased, or when nitrogen is replaced by argon in the

oxygen-inert mixture (both probably raise the flame temperature), two types of behavior are observed. For fuels of moderate smoking tendency (isobutane, 2,2-dimethylpropane, and 1-pentene), smoke-free fuel flow rises with oxygen-enrichment or argon substitution. Smokier fuels (cyclopropane, propene, and 1-butene) behave in the opposite manner at the lower oxygen concentrations; at higher enrichments, smoke-free fuel flow again rises with both oxygen content and argon substitution.

With a constant secondary-air flow rate and constant fuel-flow rate, the smoking-point fuel-air ratio of a premixed flame decreases as the tube diameter is decreased. Presumably the oxygen supply to the flame is increased, because, with the smaller diameter, the flame has a narrower outer mantle.

4. Increases in fuel temperature in diffusion flames to 190° C or in fuel-air mixture temperature to 450° C in premixed flames produce no effect on smoking tendency.

5. Maximum smoke-free fuel rate (or flame height) of diffusion flames is a linear function of reciprocal pressure over the range of ½ to 20 atmospheres. The rate of diffusion, and consequently the rate of mixing of fuel and air, may account for this relation. In premixed flames, which are nearly independent of diffusion, the smoking tendency is probably independent of pressure.

6. The flame height of premixed flames varies linearly with fuel-flow rate but, at the same time, the smoking tendency increases. This increase may be due to the decreased surface-volume ratio of the longer flames and the resulting decrease in the diffusion of oxygen into the outer cone.

7. A critical survey of the literature suggests that smoke results from partial dehydrogenation steps, followed by decomposition to acetylene and hydrocarbon fragments, which then undergo simultaneous polymerization and further dehydrogenation to form smoke.

8. Appreciable amounts of smoke can subsequently be burned in the outer reaction zone of a flame. High concentrations of finely divided smoke tend to burn in the outer cone, whereas the same amount of smoke coagulated into soot particles may not burn completely. The amount of primary and secondary air associated with a smoke-burning flame influences the size of the smoke-burning region of the flame. In general, decreasing the primary-air supply increases the size of the smoke-burning region.

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